







**LIEBIG'S**  
**QUESTION TO MULDER**

TESTED BY

**MORALITY AND SCIENCE.**

BY

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## INTRODUCTION.

INTO the subject of the following Pamphlet, in so far as it is of a personal nature, it is unnecessary for me to enter. Acquainted for many years with both Chemists, I can only regret that human feelings should be allowed to interfere so much with the progress of the science to which we are all attached,—and that the temptation to publish, which the editing of a journal affords, should have so often induced Liebig to commit to the printer expressions of a warm, hasty, and angry nature, which, upon calm after-consideration, he must have frequently wished to retract.

Of the facts contained in the subjoined pages, the reader will judge for himself. In so far as my own knowledge of the subject goes, I confess I both sympathize with the feelings of Mulder, and agree in his conclusions. Were it not so, I should have thought it unnecessary to take an interest in presenting his Reply to the public.

Two years ago I induced my assistant, Mr Fromberg, to undertake the translation of Mulder's work

on Vegetable and Animal Physiology—a work not yet completed in the original Dutch. In doing so I satisfied myself that I was rendering a service to British Science.

In the course of the present year, however, Liebig has denied the accuracy of some of the most important statements in that work—those regarding the protein compounds. I feel bound, therefore, to place in the hands of the English readers of his work the defence which Mulder has published of his own statements. That defence is such as, *in the present state of our knowledge*, fully to uphold his former experimental results and theoretical deductions, in opposition to the objections of Liebig,—and to claim for his opinions a continuation of that confidence which has already been so extensively placed in them throughout Europe and America.

The main point assailed by Liebig will be understood by the following statement :—

Mulder, many years ago, examined the fibrin of blood, the albumen or white of the egg, and the gluten of wheat. When these substances are dissolved in caustic potash, with the requisite precautions, and the solution is then made slightly acid by the addition of vinegar, a white precipitate falls, which Mulder collected and carefully analysed. To this substance, for certain theoretical reasons, he gave the name of *protein*. It was free from sulphur and phosphorus,—both of which are contained in the albumen of the egg and the fibrin of the blood. It consisted of carbon, hydrogen, nitrogen, and oxygen only, and was represented by him by the formula



By degrees, as his researches multiplied, and were enlarged and confirmed by others, his own views extended, and he arrived at the following general conclusions:—

*1mo*, That this protein formed the basis of a large group of animal substances—the albuminous group—comprising fibrin, albumen, casein, the crystalline lens of the eye, hair, horn, &c.

*2do*, That in these substances the protein was combined with oxygen, sulphur, or phosphorus, or with two of these bodies, or with all the three,—and that the proportions of these several elements determined the special qualities of each compound of the albuminous group.

*3tio*, That the sap and leaves, but especially the seeds, of plants, contained protein in combination with sulphur and phosphorus, as it is found in the animal body,—and that the gluten of wheat, the legumin of the bean, and the nitrogenous substances generally, which are found in the seeds of plants, were compounds of this kind. Lastly, he ventured to announce in a brief manner,

*4to*, That these substances were formed by the plant out of the food drawn by its several parts from the air and from the soil,—that it produced them for the purpose of diminishing the digestive labour, so to speak, of the animal—of supplying it with food fitted directly to form and nourish its muscular and albuminous parts—and that the animal derived its whole supply of the raw material out of which these parts were to be built up, from the vegetable food on which it lived.

This beautiful train of research and reasoning naturally attracted the attention of scientific physiologists,

and gave to protein an importance in the history of Organic Chemistry to which scarcely any other known body can lay claim.

It is a remarkable fact, that up to January last, the researches of all other chemists only tended to confirm Mulder's experimental results, and to strengthen and widen his deductions. The laboratories of Paris, of Giessen, and of Stockholm, had been employed upon them at intervals for several years, and yet the existence and characters of protein, as described by Mulder, were only everywhere confirmed.

But in January last, Liebig announced, in his *Annalen*, that he could no longer obtain protein possessing the composition and properties assigned to it by Mulder. He intimated his belief that the so-called protein always contained sulphur,—that without sulphur it could not exist,—and that, when perfectly freed from sulphur by the action of caustic alkalies, it ceased to possess the characters or composition of Mulder's protein. He threw doubts, in like manner, upon the existence of the so-called oxides of protein, and invited Mulder to explain away the difficulties which he now professed to meet with.

Subsequent to this, in the May number of the *Annalen*, a paper appeared by Dr Laskowski, one of Liebig's pupils, detailing the experiments to which Liebig had previously alluded, and drawing similar conclusions. Two other short memoirs in the same journal, and by pupils of the Giessen School, shewed that the quantity of sulphur previously assigned to albumen and fibrin by Mulder was too low; a fact which the newer researches of Mulder himself has established, but which does not at all affect the exist-

ence of protein, or the value of the so-called protein theory.

This statement will enable the reader to understand both the object of the following pamphlet, why it was necessary to write it, and why I think it of importance that the readers of the *Chemistry of Vegetable and Animal Physiology* should have an opportunity of perusing it. The basis of a most important theory is attacked,—the numerous and beautiful deductions drawn from it are attempted to be shaken,—and the scientific reputation of a skilful analyst is called in question. It is for the interest of science, therefore, that the truth should be ascertained and made widely known.

Of the personal matters between Liebig and Mulder, the reader will form his own opinion. Individual feelings and character may be affected by the nature and form of the present attack and defence; but truth will gain by the new researches to which the dispute has already given rise. Is it necessary, however, that the birth of truth should thus be attended by individual pain, as in the throes of human labour?

JAMES F. W. JOINSTON.

EDINBURGH, 30th October 1846.



# LIEBIG'S QUESTION TO MULDER

TESTED BY

## MORALITY AND SCIENCE.

The January Number of the "Annalen der Chemie und Pharmacie, 1846," pages 132 and 133, contains a short paper by M. Liebig, in which he states "that when fibrin, albumen, or casein, is dissolved in a moderately strong potash ley, and the liquid neutralised by acetic acid, the precipitate produced is not protein free from sulphur," *as I believe*;—"that hitherto he has not been able to obtain the substance which I have called *protein*, with either the composition, or the properties which I have ascribed to it,"—and in which he expresses a wish "*that it might please me to mention, with every possible detail, in what way I have obtained that substance.*"

Although, on the one hand, a request of this nature, in words so mild and agreeable, seems to do me much honour, being made by a man who has rendered so many services to science,—yet, on the other, it appeared somewhat strange to me, and difficult to be complied with.



This difficulty was not inherent in the subject itself, but arose from circumstances unconnected with it.

It arose chiefly from this, that M. Liebig is morbidly irritable, always seeking to quarrel, and with every body, and disputing in a way which is disapproved of by every civilized man. I am not afraid of being assailed by him; on the contrary, I should deem this to be an honour, because I should be attacked in company with the most eminent men of science. I fear neither abuse nor nicknames, which are the weapons with which M. Liebig always fights, for these only injure him who uses them. I have no fear—as is the case with many, who, for this reason, dare not speak,—of being injured by him in my social position, an object which is always aimed at by Liebig in his so-called scientific contests. I am not afraid of Liebig; I am only afraid of my own conscientiousness.

The only fear I have, in short, is, lest, in my reply to him, I might use a word which I should not always be able to defend, as most fit for my purpose; for this man, whom I most highly respect for his chemical knowledge, is, at the same time, an object of my deepest compassion. I am not personally acquainted with him; all I know of him is from his writings and his letters, and this knowledge compels me to pity him. But, at the same time, I disapprove in him what I would disapprove in myself and in every other man. All our actions have but one touchstone,—that of morality. No deviation from this can be tolerated under any pretext. That which possesses moral value, receives respect. That which ought to possess this value, but is void of it, obtains contempt. This touchstone I am bound to employ in science.

It is, in my opinion, the duty of cotemporaries to

support one another in what is good, both within and beyond the domain of science ; it makes no difference whether this good is called science or by some other name. I think it is an indication of a morbid condition of mind in a man to suppose himself called upon to judge every one from high ground, and to do this by preference in an unfavourable sense. Strong against evil,—but at the same time strong in favour of what is good,—ought to be the watchword of every civilized man, and especially of the man of science ; for if the latter is not to be reckoned among civilized men, then away with science.

I am further of opinion, that he who is still a child in regard to what is decent and due to others, has no claim to be called a great man, nor even a man of science. This decency nobody will confound with cowardice or want of principle. We ought also to distinguish when force is proper to be used, and how it should be applied. Brutality is not decency. When a man of science considers himself called upon to stand always at the whipping-post—always, and by every violent means to deal out blows, and thus to brand other men, his fellow-creatures,—such a man degrades himself in the highest degree. Every time that he is unjust, he is a forsaker of *truth*. He has no scientific sense—a sense which is known by its feeling after *truth* ; and *injustice* agrees not with *truth*. To be always striking and branding others is not to be just. It indicates a state of disease—disease which brings down the great to the little, the sublime to the base. Contemporaries pity it much, and the judgment pronounced upon such actions by posterity, expresses contempt. Paracelsus may have felt happy, in ascribing to his own cap more learning than was possessed by all the learned societies

of Europe ; but his happiness was a soap-bubble. It was a misfortune, both despised and pitied by those who have learned to understand the sentence of Erasmus : “ *Ingenuas didicisse fideliter artes, emollit mores nec sinit esse feros.*”

Liebig's restlessness in destroying his own happiness, could not fail to afflict every one who is able to appreciate his talents, although he might not see in him a man having a right to command—as Liebig does in himself ; nor the man who *alone* possesses knowledge, intellect, and a sense of truth. This restlessness has for years been to me a cause of intense grief. I have requested, nay implored him, to cease beating down every thing about him. To me he had only given, as yet, one nickname,—that of *iatro-chemist*,—and this could not certainly cause me much pain ; but I have implored him no longer to maltreat meritorious men, and have advised him, with heartfelt interest in his own life, to discontinue such intolerable conduct.

On the 12th of December 1844, I wrote him a letter, of which the following is a literal translation :—

“ I am deeply grieved that I was not honoured with an answer to my request to reconcile you with . . .  
 . . . . . Convinced as I am, that my only intention in this matter was to do good, my only idea to promote decency and probity, to join in the defence of your reputation, I persist in imploring you to blot out the stain which is so very much condemned by every impartial person. There is a class of people who never tell us the truth, but only that which is pleasant to us, whilst behind our back they speak quite differently. But I like just the contrary. A thousand times I have spoken in your defence, but I never flattered you. Listen to me, when I tell you, that though there is a

scientific glory, there is also another, of a much higher order, and much more worthy the man of mental cultivation, viz., the glory of having done what is right. After you have attacked almost the whole scientific world, you now commence attacking the men of greatest genius. Where are you to stop? And when you shall have awakened the enmity of (*perhorrescirt*) every one around you, what will you have then accomplished?

“I assure you, I seek only your happiness, your peace of mind, your glory. I could shew you several letters from so-called friends of yours, which are full of words of condemnation. They are afraid to write to *you* what they write to *me*—what they say of you. But, even although none were disapproving of your actions, lay your hand upon your heart and ask yourself, ‘Have I done right in always using so harshly every one who does not adhere to my ideas, and who does not follow my method of treating science?’ Your heart will answer, ‘Surely not!’

“Believe me once more. Your life is full of troubles—your old age will be full of vexations—and your death-bed full of remorse.

“These are, without reserve, the opinions of a man who never shewed you any other than marks of respect, who will never write against you unless you force him to do so;—of a man who is personally unknown to you, but who seeks in man first for probity, and for science only in the second place. The development of our moral powers is the purpose of our life. Both you and I—after Chemistry shall have ceased to exist for us—both you and I are bound to strive, that we may then dare to remember what we have done in this world.

“Honest Mr . . . . does not subscribe to all your ideas; he has both written so to you and has published his views in print. But in this he nevertheless remains a man of character and of good faith. I, myself, am far from agreeing with everything you have written: Am I therefore, also, not to be exempt from your personal attacks? If this is your pleasure—then be it so! But I shall nevertheless remain what I was in my own estimation, and in that of the whole world. And, even although there may be nobody who shall then dare to defend me or to take my part, I shall nevertheless remain alone with a good conscience—satisfied, happy, and calm; even without the aid of Chemistry; for these things are above all science.

“But two words more before I conclude. Perhaps this is the last time in my life that I write to you; for I am not a coward. If this is the case, then may you live in happiness, enjoy whatever is good and desirable in life, and if you should now and then remember the iatro-chemist, believe me that nothing from without can trouble him.”

Thus I wrote to Liebig on the 12th December 1844. Was I his friend, or what else than friendly could have been my intentions?

But all in vain. Since that date he has attacked many other chemists, and in a manner which excites the highest indignation. Storming and raging, his pen flies over the paper, mad with fury against every one who dares to make a single remark upon his opinions.

Freedom of scientific opinion has never been understood by Liebig. For years past a tribunal has been established in Giessen, before which Liebig is at the same time accuser, witness, public prosecutor, advocate, and judge. Before this tribunal a case is rapidly

terminated, but grace or justice can *never, never*, be obtained there. From this tribunal even the purest innocence is never dismissed without being whipped and branded; and for this purpose again Liebig holds also the office of executioner, and is never fatigued with whipping and branding. *Truth!* he exclaims, and goes on whipping; *Truth!* and down comes the rod; *Truth!* he repeats once more, while he is heating his branding-iron red-hot; *Truth!* finally, and he presses it on the forehead of the chemists of the day, and rejoices in the ascending vapour. If, perchance, this whipping and branding is discontinued for some days or weeks, then he talks of forbearance (*Annalen*, January 1846). He is, in his own estimation, a hero in the empire of morality, because he has deigned for some days or weeks to leave the rod at rest.

An unhappy spirit—truly! Science cannot exist without *liberty*. No other tribunal ought to be admitted but that of justice, and this ought never to *pronounce judgment*. An exchange, a mutual exchange, of ideas,—urged with warmth, if you will, but at the same time under the control of moral principle; this is what ought to take place before such a tribunal. He who gives judgment in science, has no sound conception of what science is. His aim is not science, but himself. To pronounce judgment, without a right to do so, is presumption—as remote from love of truth as justice is from injustice.

But does not greater capacity impart a right to give judgments in science? Liebig thinks it does. He considers himself to possess the greatest capacity that ever existed, and *he* therefore has rights possessed by nobody else.

Can there exist any greater error? As we proceed

in its development, we perceive more and more how unlimited is the dominion of knowledge, and how limited our faculties are; how great the depth of truth, and how great the difficulties which attend the attainment of it. The judgment of young men is generally bold, and little indulgent; but it calms down in course of time, and in proportion as they compare themselves with what they wish and ought to be.

But Liebig has taken quite an opposite course. Almost every one who moves on the same scientific ground with himself, has been attacked by him with a fury, such as was never exhibited in science. He leaves no one at rest; and pronounces judgment upon men and things in a manner which grows bolder, more severe, and more afflicting, as his circle of knowledge expands.

I shall quote here a few out of the hundreds, nay thousands of instances, in confirmation of the above statement.

In the *Annalen* for January 1846, p. 105, he calls Laurent "one of the most talented chemists of our time, and the most rich in genius;" and yet, on the same page, he represents him as "a stage-hero, who covers himself with gilded paper, made out of the undervalued labours of others;" while in p. 112, Laurent and Gerhardt are said to be "two conceited self-complacent cocks strutting about on the top of a dung-hill."

It is true that some individual is now and then highly praised, but only with a view to the rule: *Tolluntur in altum, ut lapsu graviore ruant*. Laurent first was persecuted for a succession of years, then he was allowed to teach at Giessen, and now he is a cock on a dung-hill. Gerhardt was first praised for his excellent trans-

lation of the *Chimie Organique* (see the preface to that translation); now he is accused of having mutilated that book (*Annalen*, January 1846, pages 106, 107). Formerly, Mitscherlich's language was scorned as *old wife's babbling* (*Ann.*, 1841, p. 358); now he is quoted as an authority against Gerhardt (*Ann.*, January 1846, p. 118), and is again "Herr. Professor Mitscherlich." And the man who, with all the wicked purpose of wounded self-love, could sneer at one whom he formerly called *the most experienced chemist of our time, and probably of all past times*—this same man now dares to write (*Ann.*, January 1846, p. 117), "that words fail him to express his indignation against Gerhardt's behaviour towards Berzelius,"—a behaviour which certainly deserves to be met with the same indignation as that of Liebig towards Berzelius (*Ann.*, May 1846, and *Comptes Rendus Complets*, Febr. 1845). This man (Liebig I mean) ought first to feel indignation against his own actions before he expresses it so warmly against those of others.

Four years ago, I myself was held up as an example to Dumas (*Ann.*, Bd. 38, s. 202.); five years ago, every thing I did was right, and all I had done had been confirmed in his own laboratory (Letter of June 1841); "but now I have contradicted him on almost every page (!) of the latter parts of my work on Physiological Chemistry\*—I hurry towards an abyss, and most of my results are false. Now my hunt after numbers has mutilated the science, and through me physiological

\* My last parts are Nos. 5, 6, and 7 (3d in the English Tr.). There occur in these parts ten pages in about 400 in which I have differed from Liebig—consequently one-fortieth of what Liebig has found. My opinion about dealers in artificial manures he could not have read, as it had not yet appeared in the German translation.



chemistry has become unworthy of confidence." (Letter from Liebig, 29th March 1846.)

In this manner Liebig has got into quarrels with every one; and a legion of pamphlets has appeared against him, in reply to his unwarranted attacks, which are always made under the mask of truth. Men, such as Mohl, who never before used the pen for any other purpose than for the quiet advancement of science, were forced to shake off the odium that was thrown upon them and their labours; and though numbers have called out to him, in their deep conviction of his errors, "Cease your injustice"—he still goes on like a madman, seizing one after another, and always under the detestable war-cry of *love for truth*.

Is such a man not to be sincerely and deeply pitied? For, who can have greater claims upon our compassion, than one who, during his whole life, has been hunting restlessly after an object from which he is continually farther removed? And is any other object allowed in science than the promotion of true civilization, of true humanity? If science is made an instrument for diffusing over the world fury and anger, then it becomes, in my estimation, a base tool, and is deprived of the noble characters by which it ought to be distinguished. Its object is *truth*; and all that belongs to the domain of truth, lies between those of intellect and morality. There can be no morality without truth, no science without truth; but, at the same time, no science, no pure science of the nobler and higher order, without morality.

The man of science, therefore, whilst advancing in knowledge, ought at the same rate to advance in the path of virtue and truth. His aim is the promo-

tion of true civilization, true morality, both in himself and in others. Whilst striving for truth, in whatever direction it may be, the image of truth appears to him in general more and more lovely. He defends it with all his power, but at the same time with the greatest conscientiousness. Thoroughly penetrated by the love of truth, searching for truth, and for truth alone, he connects with it a higher moral principle; so that whilst at first science was his only object, it gradually becomes to him—the more he penetrates into the purpose of human life—a means for higher development. He perceives the images of science and of virtue drawing nearer together, and he loves both with equal warmth. Not a means of making a vain show, or of obtaining fame, is science for him, but a means of advancing in moral worth. This appears in his whole behaviour: he is called a civilized man, and justly so, for he has really increased in worth. He elevates himself above the littleness of the world; calamities he bears with courage. And when his task on earth is finished, then—although he has scarcely entered upon the immeasurable domain of truth, into which he cannot penetrate deeper in his present abode—he leaves this stage with confidence, to build, in a future order of things, upon the foundation he has laid here. Mankind constantly blesses his memory, for, in his investigations, he has left a precious treasure to posterity.

This is the character of the man who possesses real wisdom,—of the truly scientific man. Is his character different?—then he is not a man of pure, of real science.

Three reasons move me now to call upon Liebig in public, as I have before done in private letters,—  
*“Put a stop to your injustice; do not lose sight of the purpose of your life; do not abuse science for a low end;*

*above all, be just, for justice towards men is the foundation of truth."*

\* In the first place, I am indignant at his unwarranted treatment of his cotemporaries. I deem it my duty openly to pronounce my indignation, since Liebig still continues in the same course, after my sincere and well-meant letters to him,—which I wrote merely to promote the general good, and for no reason affecting myself *personally*. He must be stopped in his course. The man experienced in science must, through science, promote the good and not the evil. I would force him to do so by moral constraint. This is my first reason.

The second is: that Liebig allows to chemists no other alternative, but either to look indifferently upon the grossest injustice, and the greatest misrepresentation of truth, or to have their characters as men of reputation, in science, destroyed by him. All this he calls *truth*. Probably the word *truth* was never written by any man so often as by Liebig; and yet, in my opinion, few men know as little about what is true as Liebig does.

No chemist of the present time can offer better proofs of this statement in his own person, than I can; and I therefore feel bound to make these proofs known.

Not for the purpose of maintaining my own reputation as a chemist; for the opinion which the public may entertain in regard to my knowledge, does not give me so much concern. It would be a small matter to me, during the few years I may yet have to live here, to be considered, in the eyes of every one, as having no knowledge of chemistry, as being a bad experimenter, and as having erred in every thing I have performed in science. I say, I am above the opinion of the multitude in regard to the amount of my scientific knowledge; and, consequently, I do not intend to enter into

a pleading with the man of *Giessen* before the tribunal of the public. On the contrary, every time I see this done between him and others, it serves me as a proof that Liebig mistakes the purpose of his own life.

But all that has happened between Liebig and myself for some years past, convinces me that his object is not truth, but himself, and that he uses the word *truth* merely as a shield, behind which he may fight with safety. Now, this is not only an ignoble way of acting, but it is injurious, in the highest degree, to the young chemists of the present century. I am called to join in the maintenance of the pure conception of the object of science during the time in which I live—to preserve it from pollution;—and therefore I feel obliged to bring under the notice of others some of the things which, as a man of science, I have experienced from Liebig. Especially I wish to bring them under the notice of Liebig himself, that I may compel him, by moral constraint, since I could not bring him back from his evil ways by friendly requests. Liebig must cease to be a stirrer up of strife, and must either become an honest chemist, or lay down his pen.

But besides these two reasons, there is a third one, which concerns myself as a man. Every one has a right, nay is obliged to keep his name, as a *man*, unstained. Liebig respects *nobody's* name, moral character, social position, life, or health. When I began to rise in public estimation, I also became an obstacle to Liebig,—I became an obstacle in the earning of the whole of the glory that can be obtained in the prosecution of chemistry—which is to be reserved entirely for Liebig, and for such as Liebig thinks fit to share it with.

When my work on Physiological Chemistry was about to be published in Germany, without my interference,

I said to my friends, "Liebig will not bear this. The publication of this work will bring me also into the class of those who are to be destroyed by him." I had seen this to be the case with so many others, whose position as chemists is not an obscure one, and who do not keep off the ground upon which Liebig moves. Now, I had not placed myself upon his ground, but Liebig had entered upon mine. Consequently, it became his ground, and I had to be removed from it.\*

Every one who contradicts him in science is a bad man, and must be destroyed. Now I have contradicted him here and there, and, consequently, I am a bad man, and must be destroyed. He who gives him no honour, and is not always speaking of Liebig as the sole chemist (*den eenigen Liebig*), is immoral, and must be destroyed. I have never done so, and, consequently, I must be destroyed. This attempt at destruction commences by quarrelling about some slight matter in which he appears to have justice on his side—and soon the whipping-post shakes with the furious blows inflicted upon the wretched being who has been bold enough to make a remark upon the sole man (*den eenigen man*).

As for me, I am indignant at the language and conduct of Liebig towards others. This indignation was apparent in my letter of 12th December 1844; it has remained with me till this moment, and has been raised to the highest point by the language he has since addressed to others,—by the unwarranted language, for instance, with which, in the same periodical in which he puts his question to me, he addresses Gerhard and

\* The meaning of this is, that the peculiar walk in organic chemistry which Mulder had chosen was quite distinct from that to which Liebig's researches were confined, and that Liebig latterly has chosen, along with his pupils, to enter upon that walk.—T.

Laurent,—two chemists personally unknown to me, but who are, nevertheless, his *fellow-men*. This question to myself requires elucidation.

In answering it, shall I address him in *his own* style,—with invectives and nicknames? Far from it. I will address him in the same style in which I wrote him on the 12th December 1844. Though doing me the greatest injustice, though ever seeking cause for quarrel—of which the protein question, now again brought forward, is a new proof,—he shall not have occasion to say of me, that I have not respected in him *those* talents which are peculiarly his own, although I deeply regret that he so often abuses them. I will address him in a manner to which human rights entitle and force me. I will teach Liebig that he who is *unjust* is unacquainted with *truth*, however frequently that word may be upon his lips.

These words of mine, therefore, are not to be considered as a polemic pamphlet, but merely as the utterance of my profound conviction of Liebig's thirst for the opposite of truth, and of his morbid scientific feeling; not as a contest with Liebig, none at least between me and him, because I am averse to storming and raging.

As regards the protein question, it is one of the many from which Liebig's sense for truth may be learned. "He has hitherto not been able to obtain the body which I have called protein, either of the same composition, or with the same properties, as I have ascribed to it." Let us examine what degree of truth is contained in these words.

### 1. *The Composition of Protein.*

With regard to this point, one of Liebig's pupils,

under Liebig's own eyes, analysed protein, and obtained results which are everywhere praised by Liebig (Ann. xl., p. 39, xxxix., p. 134), and agree completely with mine, Thus:—

Protein analysed by me (1838, Bulletin, p. 110),  
C = 76.437, gave

From Fibrin.	From Albumen
G 55.40	55.30
H 6.95	6.94
N 16.05 (calculated)	16.02
O 21.56	21.74

Scheerer, Liebig's pupil, obtained (Annal. 1841, xl. p. 44), C = 76.437

From the Crystalline Lens.	From Albumen.	From Fibrin.
G 55.30	55.16	54.85
H 6.94	7.05	6.96
N 16.22	15.97	15.85
O 21.54	21.82	22.34

It would, therefore, have been but just, I think, if Liebig had put the question concerning the *composition* of protein not to me, but to Scheerer, whom he calls, rightly in my opinion (Bd. xxxix. of the Annalen, p. 134), “an experienced and talented chemist and physician,”—to Scheerer, who seems to have perfectly succeeded in preparing from the crystalline lens, from albumen and fibrin, a substance of exactly the same composition, and not in the least differing from that which I had found before;—to Scheerer, who has worked under Liebig's eye, and by Liebig's advice;—to Scheerer, who appears to have actually obtained in 1841, what Liebig says he has not yet been able to obtain in 1846.

A person who is unacquainted with the human heart, cannot comprehend Liebig's request about the *composition* of protein, and the less so, since the

the results obtained by Scheerer in Liebig's laboratory agree more completely with mine than could be the case with any other substance. We both found 55.4 — 54.8 of carbon, 7.0 — 6.9 of hydrogen, and 16.2 — 15.8 of nitrogen. Scheerer prepared the substance exactly in the same manner as I had done, and every one will therefore acknowledge that Liebig might readily have either informed himself, or have asked Scheerer, how this substance could be obtained *of a constant composition*; or still better, might have remembered how Scheerer, five years before, had prepared it under his own eyes.

It is indeed notorious, that Liebig appropriates to himself the labours of his pupils; that he makes it appear to the world as if all the talents of those who go to Giessen to study practical chemistry, were concentrated in his own brains; and that, with regard to our present subject, he has also brought it forward, as if the whole investigations had originated and ended in him and his own laboratory. By doing so, Liebig has, at the same time, brought upon himself the necessity of standing forward as its defender against all attacks from others.

He who appropriates to himself the honour of a discovery, and afterwards calls upon another, whom he has deprived of it, to account for its accuracy, is, in my estimation, an unjust man, and, consequently, a man unacquainted with *truth*.

Now I granted the honour to Liebig,—I grant him all honour,—but he must allow me also to decline the defence of stolen goods. For what reasons induced Liebig himself, from the results of Scheerer's analyses, to calculate for protein the formula  $C^{48} H^{86} N^6 O^{14}$ ? (Annal., vol. xl., p. 44.)



He calculates protein thus,—

	Per Cent.
C 48	55·742
H 36	6·827
N 6	16·143
O 14	21·288

These numbers are neither Scheerer's nor mine; they belong to Liebig alone; and that they have been taken, not from my analyses, but from those of Scheerer, I think appears from p. 44, vol. xl. of the *Annalen*.

I can understand the whole affair if Scheerer be also among those that have fallen into disgrace. But if he be still numbered among Liebig's friends, I then advise Liebig to consult his own memory, and ask himself how, after calculating, five years ago, a formula of his own, from analyses made under his own eyes, he can *now* ask by what process it is possible to prepare the body in question?

If Liebig, however, obtains no assistance, either from his own memory or from Scheerer, he will do well to address himself to Dumas, with whom he was to work out organic chemistry, and to consult his treatise, *Sur l'état actuel de la Chimie Organique*, communicated to the French Academy on the 23d October 1837.

Dumas, who is far from being a friend of mine, has, in concert with Cahours, obtained results from protein, which agree both with mine and with those of Scheerer, to which Liebig formerly adhered. To make the comparison easier, I shall assume the equivalent weight of carbon to be 76·437, instead of 75, as was done by Dumas and Cahours. Their results were,

	Protein from	
Casein.		Albumen.
C 55·29		55·42
H 7·11		7·14
N 15·94		15·92
O 21·66		21·52

—(Journ. de Pharm. et de Chim. III., p. 11-12.)

Dumas observes: "Comme nous attachions une grande importance à ces analyses, on a pris toutes les précautions imaginables pour en assurer la parfaite exactitude." This does not certainly signify much from the mouth of Dumas, and I do not quote it for that reason; but, as connected with an affair of mine, it alters the case materially. (Oil of cinnamon.)\*

It was remarkable how Liebig and Dumas at that time (1842), disputed the honour of having found the formula  $C^{48}, H^{36}, N^6, O^{14}$ . This formula, it was stated, had been constructed by Liebig "from the composition of choleic and uric acids; it did not express an atomic weight, and was called a formula for fibrin and albumen." (Annalen, vol. xli., p. 355.) Dumas was said "to have appropriated it from Liebig, and to have probably obtained it through Marignac, (*Ibid.*, p. 352). But Liebig calculated  $H^{36}, O^{14}$ , and Dumas  $H^{37}, O^{15}$ . Curious facts these! A formula derived from choleic acid,—of which the composition is entirely different from that assigned to it by Liebig!—Dumas and Liebig quarrelling about a formula which did not express the composition of fibrin and albumen,—of which the sulphur and phosphorus had not yet been determined,—but of *an organic group*, contained in fibrin and albumen! Liebig accusing Dumas of having robbed him of the honour of this discovery *at the end of February 1841!*

This, therefore, was sense for truth! I observed it with amazement, and was, at the same time, even more astonished, when Liebig wrote to me, saying, "that he was the first who had done justice to my labours, which had for years (?) been lying unobserved in

\* The allusion here is to a difference between Dumas and Mulder, in reference to the true composition of oil of cinnamon.—T.

the work of Berzelius." Dumas and Liebig quarrelling about the formula of a body, which, according to Liebig, was composed in the hundred parts of ( $C=76.437$ ).

C 55.742  
H 6.827  
N 16.143  
O 21.288

Quarrelling about the priority of its discovery ;—and now asking a person in Utrecht, "to mention, with full details, how this body is to be prepared?"

This is truth and justice !

In the "Bulletin de Neêrlande," p. 112, published on the 30th July 1838, and forwarded, a few days afterwards, to Liebig and Dumas,—to Liebig directly, and to Dumas through the French Academy,—some statements of mine are found, which I shall here transcribe. After the conclusion that, by treating Beccaria's gluten from wheat, with potash and acetic acid, a body of the same composition was obtained as from fibrin and albumen, I wrote as follows :—

"Il paraît donc, que les animaux tirent leurs principes constituants les plus essentiels immédiatement du règne végétale. Il se peut que l'albumine végétale contienne le soufre et le phosphore dans une autre proportion, que l'albumine animale, la fibrine, etc., mais le corps organique quaternaire est la protéine même.

"Les herbivores ne sont donc, sous ce point de vue, pas différens des animaux carnivores : tous deux sont nourris par la protéine, par le même corps organique, qui est un principe principal dans leur économie.

"Le pouvoir nutritif du pain et des autres alimens, qui contiennent de la protéine, est donc bien facile à concevoir. Ils fournissent, sans que la digestion y

opère quelque changement, immédiatement une des parties les plus essentiels du corps animal.”

The reader, who knew that Liebig and Dumas were, in August 1838, acquainted with these statements, and also with the grounds upon which my conclusion was based;—the reader, who thereafter, in 1841, heard Liebig loudly proclaiming:—“ I, Liebig, have taught the world that the principal food of animals is prepared by plants;” and who heard the same thing loudly proclaimed by Dumas one year later still, viz. in 1842:—“ I, Dumas, have taught the world that the principal food of animals is prepared by plants;”—this reader cannot but join in my wish, that one of these days Dumas may also come forward, as Liebig has done, and ask me, “ How have you prepared that body, for which, as *our own discovery*, we assumed the composition—

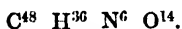
I, Liebig.		I, Dumas.	
C	= 76.437	C	= 75
O 48	55.742	C 48	54.44
H 36	6.827	H 37	6.99
N 6	16.143	N 6	15.88
G 14	21.288	O 15	22.69 ?”

If Dumas were now to put the same question to me, then truth were perfect, and justice complete.

But every reader, who is really anxious for truth, will acknowledge that a person like Liebig, who, in all his writings since 1840, uses the discoveries of others, and appropriates them to *himself*, is a stranger to *truth*.

I am aware that Liebig has, in most cases, spoken of a formula for fibrin and albumen,—for it was not *he* who had first enunciated the term Protein, and this, therefore, was not to be used too often;—but at p. 44 of the *Annalen*, vol. xl., is the following plain statement

by Scheerer. Prof. Liebig has assumed for this body—protein,—an empirical formula, derived from the analysis itself. This formula is—



Liebig, therefore, distinguished in the vegetable and animal nitrogenous substances, not these substances themselves, but the protein. Thus the man of truth has, in all his subsequent writings, spoken what was not true, viz., that he was the discoverer of the above mentioned similarity. "I say, it was *my* researches." (Liebig, *Annal.*, vol. xl., p. 353.)

The author of a truth, then, is not he who merely gives it utterance, but he who loudly proclaims it;—not he, who writes it in *eleven lines of a quarto volume*, but he who writes whole books on the subject. This is Liebig's way of reasoning.

To me it is a matter of indifference. I leave the question of priority to people who are acquainted only with Liebig's variety of truth. To me it is only ridiculous. But he who robs a man of what is considered a distinction, should not have the boldness to address questions to *him* whom he has robbed. Others may answer Liebig and Dumas on the subject of protein; *I* will not do so.\*

\* This question of Liebig has already been presented in a different and more caustic manner than it appears in the *Annalen*, by some person who expects that Liebig will correct the numerous errors which I have introduced into animal chemistry by protein, which he prepared, not at the ordinary temperature, but by boiling in potash (*London Medical Gazette*, March 1846, p. 440). This article is not by Liebig himself, but is written in his spirit. It is stated there that I have represented protein by the formula  $\text{C}^{48} \text{H}^{36} \text{N}^6 \text{O}^{14} = \text{Pr}$ ; the intermediate coat of the arteries, by  $\text{Pr} + 2 \text{HO}$ ; hair by  $\text{Pr} + \text{NH}^3 + 3 \text{HO}$ , and further, with a sign of exclamation, "*or an ammoniated tritoxide of protein!*"

The reader may judge what degree of *truth* prevails in *this* article.

In Liebig's reply to Dumas' justification of himself against the charge of plagiarism (*Annalen*, vol. xl., p. 353), a remarkable expression occurs. After having said "that the discovery of protein is one of those of the greatest importance and most fertile in results," Liebig writes: "*It was my researches which proved that vegetable albumen, fibrin, and casein, are identical in composition with the constituents of blood;*" a statement entirely without foundation, and of which I shall presently shew the complete fallacy;—a statement, *which even Liebig himself never considered true*, but which he has made only, 1st, Because he wished to speak as little as possible of protein, which was not one of his discoveries; and, 2d, In order to produce an effect at the expense of truth.

He proceeds, thus: "M. Mulder certainly obtained protein *before me*, as a product of the decomposition of vegetable albumen; *but horn also, when treated with potash, yields protein*, which does not, however, warrant the conclusion that horn is identical with fibrin or albumen."

An important sentence, indicating the character of the man, and elucidating what he writes even now. That word "*protein*" has, from the first, offended Liebig,—because he wishes to appear the author of the theory that plants prepare the principal part of the food of animals. Now, I had promulgated that principle in 1838, and connected it with protein. *For this reason* Liebig introduced, in 1841, the poetical names of *vegetable fibrin* and *vegetable casein*, that is, the poc-

I am to be made accountable, not only for the experiments from which Liebig has derived the formula  $C^{48}H^{30}N^6O^{14}$ ; but for the formula itself, and the conclusions to which it has led him. Again, a new kind of *truth and justice!*

tical identity of the vegetable with the animal albuminous bodies ; for then they could be called " my researches : " *For this reason*, also, protein was, from the first, to be undervalued, and, in most cases, though not always, to be considered *as a product of decomposition*,—as ammonia is produced from the destructive distillation of animal substances. Protein being placed in the background, and the identity of animal fibrin and casein brought prominently forward, the whole of the merit became *his*. See, in this, says Liebig, the character of a great and truth-loving man ! Could I envy this man such enjoyment ? I allowed him to be happy in his poetical vegetable fibrin and casein ;—happy in his attacks upon protein,—which appeared at one time as *a product of decomposition* (above, p. 23), at another *as an independent organic group existing in the albuminous substances*,—that he might afterwards retract with honour.

But the following is the main point : Who says, " but horn also, when treated with potash, yields protein ? " Who says this in the April number of the *Annalen* of 1842 ? Liebig, therefore, may be asked, In what manner have you obtained from horn a substance which you call protein ?

Finally, as to the words *before me*, I cannot take them in any other sense than that I *first* obtained protein, and afterwards Liebig also. Or, if Liebig has never prepared protein, then the expression *before me* is nonsense. If he has prepared it after me, as is apparent from the expression *before me*, it is unnecessary for me now, at the expiration of four years, to tell him, " Do so and so, and you will obtain protein. "

The question put to me sounds still more strange if we consider that I have prepared protein from two

animal and one vegetable substance only, viz., from *fibrin* of ox-blood, from *albumen* of eggs, and from the *coagulated albumen* of wheat, while Liebig afterwards himself saw protein prepared by Scheerer, not only from *fibrin* and *albumen*, but also from the crystalline lens, from horn, and from hair.

Scheerer, in the *Annalen*, vol. xlix., p. 60, gave for (C = 76,437)

Protein from Hair.			From Horn.	
G	54.746	55.150	55.408	54.291
H	7.129	7.197	7.238	7.082
N	15.727	15.727	15.593	15.593
O	22.398	21.926	21.761	23.034

Dumas and Cahours prepared it from *albumen* and *casein*. I therefore prepared protein from three substances, Scheerer from two of these three, and from three others besides, which I have not used. All that remains for me, then, is to give an account of my method of preparing protein from albumen of wheat. The rest remains to be accounted for by Liebig himself, who formerly not only approved of Scheerer's analyses, but everywhere preferred them to mine, according to *his invariable* mode of doing justice. It is at least certain, that Liebig is responsible for the knowledge of *protein from horn*, and, therefore, of protein itself, since he writes, not only *before me*,—*but also that horn, when treated with potash, yields protein*.

All this at the time had its effect. Liebig thus became *the* physiological chemist. And now, from a desire for controversy, because "I have contradicted him on almost every page (?) of my work on *Physiological Chemistry*" (as he says in his letter of 29th May 1846), he must overthrow protein itself. It had its effect,



and this overthrow may produce the new advantage of placing another cotemporary chemist "in the same class with Gerhardt and Laurent;" and, as he dares to express himself, "*of making him hurry into an abyss.*" ("Dass sie einem Abgrund zu eilen." Letter 29th May 1846.) I say, *of making him hurry*, for I do not of my own accord run into an abyss. Liebig, therefore, would drive me into it. What a spirit! and also what presumption!

It is, therefore, in my opinion, as clear as daylight, that the question at issue lies not *in* the protein, but is personal, and unconnected with it. Who can shew, in the science, another question of the same kind?

But let us see how the matter stands with the albuminous substances.

After I had published my analyses in 1838, Liebig induced Vogel to repeat them (Annalen, vol. xxx., p. 22), "and assisted him with his advice." My last results were published in the Bulletin 1838, p. 108, and 1839, p. 10, and were as follow, (C = 76.437)

	Fibrin.	Albumen from Eggs.	Albumen from Serum.	Casein.
C	54.56	54.48	54.84	54.96
H	6.60	7.01	7.09	7.15
N	15.72	15.70	15.83	15.80
O	22.13	22.00	21.23	21.73
Ph	0.33	0.43	0.33	
S	0.36	0.38	0.68	0.36

My former results were—C = 76.437 (Bulletin, 1838, and Natuur-en-Scheikundig Archief, iv., p. 272 and 316):

	Fibrin from Ox-blood.				Albumen from Eggs.	
C	53.395	53.366	53.255	53.476	52.98	53.960
H	6.828	6.837	6.952			7.052
N	15.462	15.468	15.719			6.812
						15.696

	Albumen from Serum.			Albumen from Silk.
C	54.398	53.83	54.31	54.005
H	7.042	7.23		7.270
N				15.456

I had not then determined the sulphur and phosphorus, and what was wanting to make up the 100, I calculated as oxygen. In the first mentioned analyses (which were my last), I had mixed the oxide of copper with oxide of lead, by which means the combustion was rendered more perfect; and the results thus obtained I had taken in preference to those which I had obtained and published before.

Now what were Vogel's results, which Liebig had published in his *Annalen*, and which were obtained under his own eyes? (*Annalen*, vol. xxx., s. 35.) They were the following:—

	Fibrin.	Albumen.	Casein.
C	53.76	53.08	52.53
H	7.27	6.92	7.82
N	18.59	16.78	16.20
O	20.38	23.22	23.45

Vogel had used for the carbon, hydrogen, and nitrogen, the same equivalent weights as I had done; and in order that my results, upon which these experiments of Vogel had thrown suspicion, might be rendered still more questionable, it was said, at p. 22 of the *Annalen*, "that generally they agreed well with mine, but that, where Vogel differed from me, *it was not without sufficient grounds*, and careful testing."

I made no reply to this, although nobody could as yet come to any other conclusion than that the whole question was still based on very loose grounds. Differences of 0.7 per cent. of hydrogen, and 2.5 per cent. of nitrogen! Had any one else ventured to publish such results in contradiction of Vogel's experiments,

Liebig would, with all his usual violence, have pronounced anathema against such a chemist.

I would call to recollection the history of pectic acid, which Chodnew, under the eye of Liebig, certainly improved, but he found the truth *with the pen and not by experiment*. In the paper of this chemist, my analyses of the salts of pectic acid, *which are all correct, and agree with Chodnew's own experiments*, are nevertheless *said* to have contained an error of 3 per cent. in the carbon. (Scheik. Onderz., Deel ii.) Truth and justice!

And what became of Vogel's numbers, found *under the eye of Liebig*?

Two years later, Scheerer obtained, *under the eye of Liebig, in Liebig's laboratory, and aided by Liebig's advice, as before*, other results, perfectly agreeing with those of my last experiments. Scheerer found, namely (Annal., vol. xl., p. 34, 38, and 41), C = 76·437 :

FIBRIN.				
C	53·671	54·454	55·002	54·976
H	6·878	7·069	7·216	6·867
N	15·763	15·762	15·817	15·913
O	23·688	22·715	21·965	22·244
S				
Ph				

ALBUMEN.				
C	53·850	56·461	55·097	55·000
H	6·983	7·201	6·880	7·073
N	15·673	15·673	15·681	15·920
O	23·494	21·665	22·342	22·007
S				
Ph				

CASEIN.				
C	54·825	54·721	54·665	54·580
H	7·153	7·239	7·465	7·352
N	15·628	15·724	15·724	15·696
O	22·394	22·316	22·146	22·372
S				
Ph				

Are these analyses so much better than mine? Every just man will say, No. But they are, nevertheless, intended to confirm mine. What would Liebig have said, if I had published analyses by one of my pupils to test researches of his? And does not justice require that we should treat others as we would wish to be treated ourselves? He who is of an opposite opinion expresses, by this alone, that the words truth, uprightness, and justice, are mere sounds. Justice is the same for Liebig as for every other reasonable being.

Uprightness required, that the man who had the same substances analysed for the *second time*, under his own eyes,—who preferred the last obtained results, and copied them into his books, should have added, “I did an injustice in considering Vogel’s experiments in my *Annalen* as a proof against those of Mulder; this injustice I hereby wish to correct.”

I, however, cared little about the matter, and have suffered five years to elapse without speaking of it.

While, on the one hand, I believe that differences exist between fibrin, albumen, and casein; Liebig, on the other, asserts, everywhere and always, that they are of the *same composition*; and farther, that the vegetable nitrogenous bodies, formerly called *albumen*, *coagulated albumen*, and *legumin*, should be named *vegetable albumen*, *vegetable fibrin*, and *vegetable casein*, for the purpose of expressing their identity with each other. All gradually became one; all these bodies *had the same composition*. That is to say, they contain the same quantities of carbon, hydrogen, nitrogen, and oxygen, and of sulphur and phosphorus as well, if these two latter are present. The properties of fibrin, albumen, and casein, differed from each other, but those of animal fibrin were the same as those of the

vegetable fibrin, &c. It is stated, moreover (Annalen, January 1846, p. 133), that the "*composition* of legumin does not differ from that of the other nitrogenous vegetable substances which contain sulphur."

In another place, he expresses himself thus on the same subject.

A chemical examination of the three substances mentioned (viz., coagulated-vegetable albumen, vegetable albumen, and legumin), has led to this important result, "*that they contain the same organic elements in the same proportion by weight* ; and what is even more remarkable, that they are identical in composition with the principal constituents of blood, viz., fibrin and albumen." *It is worthy of special attention that he meant here by the same composition*, not merely a similar composition (nicht bloss eine ähnliche gemeint is), but that "*no difference can be detected in their proportions of phosphorus, sulphur, bone-earth, and alkalies.*" (Organ. Chemie, in ihre Anwendung auf Physiologie und Pathologie, 1842, pp. 48, 49).

Now this is called truth ! In 1842, the proportions of phosphorus, of sulphur, and of bone-earth, in vegetable albumen, or in coagulated albumen, were unknown ; and none of them contained any alkalies. The above assertion was supported by *no* experiment ; and consequently *it was a truth for which there was no semblance of foundation*. Liebig acknowledges in Liebig alone the right thus to handle truth. *It is therefore worthy of special attention*, that this whole assertion was an *untruth* in 1842, that it is still so, and that it will always remain so. Liebig was aware of this when he wrote it ; he was aware that there was not a single proof for it ; the statement was made merely for effect. He wished to express that the constituents of blood

were formed by plants, without naming the word *protein*;—that *the animal organism was a higher plant* (*Ibidem*, p. 50); and that everything in the animal was a product formed first in the plant. But the *substance of the cells and membranes of the nerves and brain is not prepared by plants* (*Ibidem*, p. 51). *The cells and membranes!*—to shew distinctly, that he possesses not the least knowledge of the animal organism. The *albuminous matter* of the *nerves and brain* is *not* prepared by the plant, but all the other albuminous matters of the animal organism are so prepared!

What must become of science, if it is so wantonly mutilated; if poetry is to be substituted for facts, and if that poetry is to be decorated with cells and membranes, with parts of nerves and brains, that are not prepared by plants? A sad sight it is that Liebig kindles in that dark room (*Annalen*, vol. xlii., p. 310). It seems to me as if I were witnessing the funeral ceremony—the interment of the science of living nature!

So stood the matter in all the treatises and works of Liebig since 1840: *all these bodies have been considered identical with each other*. But now all at once there arises a doubt about a precipitate, which is obtained by adding acetic acid to a solution of these substances in potash. That precipitate was found by myself, by Liebig—(*vor mir*, before me\*)—by Schœerer, and by Dumas and Cahours, to be of the same composition, whether prepared from a solution of fibrin, albumen, casein, crystalline lens, vegetable albumen, hair, horn, &c. Liebig himself calculated a formula for this precipitate, which, without any reason being assigned, was different from that for which I had already given my reasons. “No!” Liebig now exclaims, “all indeed are identical—fibrin with casein, albumen with gluten

\* Liebig's words.

—yet that precipitate, *that so-called protein*, I have hitherto not been able to obtain of the composition which Mulder (and Liebig—*vor mir*—I add) has assigned to it.” “*It was my researches*,” he called out to Dumas (Annalen, vol. xli., p. 353), which shewed that fibrin and gluten, and all the other substances, were identical, and had the same composition. But as to *that precipitate* which formerly also had the same composition, he now says,—he cannot obtain of *the same composition*.

What Liebig means by the expressions—*the same composition*, and *not the same composition*—I cannot understand. Both expressions are found on p. 133 of the January Number of the Annalen for 1846. It is said of legumin: “that its *composition* does not differ from the other nitrogenous sulphuretted vegetable substances, appears simply from this.” And six lines below, it is said of that precipitate, *obtained in the same manner from these identical vegetable substances*—“I have not hitherto succeeded in procuring a substance free from sulphur, with the *composition* and properties of the so-called protein of Mulder.” If we now leave that sulphur out of the question for a moment, there is every reason to suppose, that *the same substances*, treated in *the same manner*, ought to yield *the same products*.

Liebig alone, who considers everything belonging to the protein class to be identical, has thought it necessary, and he was obliged to think so, that this precipitate must always have the same composition. None, however, who remember the experiments of Scheerer upon hair, made at Giessen; or of Van Laer and Tilanus, upon hair and horn, can be of this opinion. Who has ever asserted, that every substance belonging to the protein family ought always to produce the same sub-

stance, when treated with potash and precipitated with acetic acid? Not I certainly, since I have myself stated in my work on 'Physiological Chemistry, that from whalebone, according to the experiments of Van Kerekhoff, and from horn, according to those made by Tilanus, no protein is obtained in this manner, but that the substance which is thrown down may be considered as a product of the oxidation of protein. Liebig denies, therefore, what he ought to assert, but I deny that I have ever said what Liebig would put into my mouth. At present, however, I go much farther than before, and I assert, that by means of *stronger* alkaline solutions, a great number of protein compounds can be made to yield protein of the same composition that I have assigned to it, even though they contain bi-oxide of protein.

Though all chemists were opposed to this position, —though no one were able to confirm it,—Liebig, who considers the so-called nitrogenous sulphuretted vegetable and animal substances as having all *the same composition*,—Liebig, at all events, has no right to come forward against this *precipitate*, unless he first recall the words "*the same composition*," which he has so frequently pronounced.

There is, however, something so peculiar in the question now broached by Liebig, that I am unable to comprehend it—even when I leave alone his position, that the so-called protein compounds are one and all the same, and assume that there are *accidental* differences among them (fibrin, albumen, casein, gluten, vegetable albumen, coagulated vegetable albumen, legumin, crystallin, globulin, horn, hair, &c. &c.), while all agree in their *chief properties*. That a general connection exists between them, is a conclusion which cannot be contested.

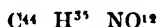


Whence could this connection arise, but from the presence of one substance common to all? a substance possessing the same composition and properties. Now I have found that this substance has no other composition than that of the body which has been called protein; this might indeed, *à priori*, be deduced by approximation, from the analyses of fibrin, albumen, casein, vegetable albumen, &c. I repeat, *by approximation*. I think also that it is impossible to establish the approximate composition of any substance so firmly as that of one which can be tested by the composition of so many other bodies.

It should have been the duty of a man of so much experience as Liebig, to ascertain the circumstances under which a body—obtained before him, and to be found after him by every one who will look for it—could be prepared, not approximately, but accurately. It is well known that none can find but he who *will*.

Should any person suppose me to assert that the composition of protein is firmly established, he would fall into a grave error. In the first place, may I ask, How the composition of a body, hitherto so imperfectly examined, could be considered as established? In the second place, we have not here to do with a substance that can be purified by repeated crystallization, but one which is most prone to transformation under the influence of various reagents. Who can say that he has duly studied these influences? I am the first to admit that *our knowledge of this substance is yet in its infancy*. But is this a reason for rejecting as false all that is hitherto known concerning it? or for calling the results hitherto obtained disgraceful? even although more recent or better investigations should extend our knowledge of the subject, and bring it nearer to the truth. For instance, are we to say that Liebig

purposely uttered falsehoods, because Regnault has corrected his analyses of the vegetable alkalies? Are Enderlin, Demarcay, Dumas, Theyer, Schlosser, and Kemp, all men who speak falsehoods, because none of them has been able to discover the composition of the so-called choleic acid? Is Liebig one who designedly uttered falsehoods, because he asserted that fresh bile can be completely thrown down by lead salts?—because the incorrect experiments with bile, made either by himself, or under his eye by young men, whom he causes to fight for him, are made the foundation of his own erroneous conclusions? or because he establishes the formula



as representing the composition of the so-called choleic acid, and indulges in innumerable reasonings upon it, all of which are incorrect? No, indeed! they were errors to which Liebig is subject in common with every other man, and such as he often commits, especially when he attempts to carry all before him by violence;—for it is not by the ferocity of a savage, nor by destroying, tearing in fragments, and abusing, that truth is discovered, unless perhaps by accident. Truth is too sublime for this. The exalted is far remote from this, and cannot be reached by means of it.

He who, with honesty and with such knowledge as he possesses, seeks for a thing, and communicates to the public what he has found, paves the way for others, although he may not himself discover the truth.

I, consequently, from the moment when better investigations shall appear, will no longer defend the composition of protein, as resulting from the analyses of Scheerer, Dumas, Cahours, and myself; but till

then, I adhere to it. (The Chemistry of Veget. and Anim. Physiol., p. 294.)

From Liebig I expect no other corrections than such as are accidental.

Every one has learned the value of the means by which Liebig pushes his ideas into the world. With unequalled positiveness is everything expressed which occurs to him *to the moment of publication*. The old is passed over in silence. But others have not, therefore, forgotten it; and when we examine the history of Liebig's scientific career, glancing over the Annalen,—that scaffold for the chemists of the present day,—the impartial reader will find that Liebig is, like every other man, subject to errors, sometimes of a grave nature; and that, whilst making mistakes which he would severely reprimand in others, he only differs from others, in thinking himself infallible. When Liebig, therefore, comes forth, or rather makes another come forth, *for the third time*, to oppose my numerical results, he must not suppose that the *third* results are necessarily *the best*. Of the whole series of protein compounds, analysed under Liebig's direction, no single result has yet been arrived at, more correct than mine; for, in most cases, the mean of all these results expresses each individual one of mine. If that mean result, therefore, is correct, each one of mine must be correct also.

Liebig himself has acknowledged, in all his writings, that my results *have been confirmed* by several young chemists, whom he himself eulogised; and any blame, therefore, which he might cast upon me in future—as he writes me in his letter of 29th May 1846,\*—I should have the honour of sharing with Liebig himself.

\* "You must not be surprised when I shall tell you all this in public."

Contrasted with him, therefore, I should have no reason to be ashamed.

But setting the question of blame aside, I am myself of opinion, that all, both of Liebig's work and my own, that has been done, up to the present time, will be improved; and if my work is corrected a little more than his, let it be so. *I have never set up claims to infallibility.*

Our knowledge of the protein compounds is in its infancy. Every one who can enlarge this knowledge does a useful work, and confers a benefit upon science. If I may take the liberty, then, I would address to the educated chemist the following invitation: *Correct my labours, and extend them, that they may gradually encircle a greater part of the domain of science than they do at present. Scarcely the first stone of a grand edifice has been laid. Reform my errors, purify science from these errors, and I especially will be grateful to you.*

After the above explanations, it will certainly be considered very strange, that Liebig ventured thus to write to me on the 29th of May last, "If you look back a few years, you will find that I (Liebig) was the first to do justice (!) to your researches upon animal substances. Your results had for years (!) been published in Berzelius's work, and no person understood their meaning. I still think myself fortunate that it was I (Liebig) who first turned the attention of chemists and physiologists to them." (!)

How am I to understand this? *Liebig even now thinks himself fortunate* that he has turned the attention of chemists and physiologists to results which are so incorrect (that is to say *at present*, for before, *they had all been corroborated*), that most of them appear to be *false*. The letter continued, "What we want is not supplied

by your analyses, of which time will shew that the greater part (*all was blotted out*) are false." If the latter statement be true, what ground was there for Liebig's *happiness*, because *he* had fixed the attention of chemists upon these *false* results? Can it be called *justice*, when *false* results are presented to the world as accurate?

Liebig ought, *therefore*, *either not to have thought himself still fortunate*, or, if he had reason for such a feeling, ought to have found for his happiness a more secure foundation than my analyses.

But, on the other hand, what arrogance is this! As if truth did not propagate itself! What does Liebig call justice? To write poetically upon a subject, and to create a sensation in the world? Unhappy man, who in science looks so much without, and so little within! He who desires to look for truth, is satisfied *when he has found it*. I was satisfied, completely satisfied, when I had made some researches, of which Liebig now speaks as if *he* were the man who has made me happy in their notoriety; and then he loudly proclaims them as "*my—Liebig's—researches*" (*meine—Liebig's—Forschungen*). But even if Liebig had proclaimed them as *Mulder's researches*, of what benefit would that have been to me? The man of science is fortunate even though no one does justice to his discoveries. This now is Liebig's way of thinking, represented by himself. To earn fame, and to collect spoil, is to his pen science and justice. It is not *truth*, therefore, which he calls justice, *not science itself* which he seeks, but its *acknowledgment* by others. And when Liebig then appropriates to himself the discoveries of another, and proclaims them as his own, this other must still be grateful to Liebig. If now, beside the peculiar kind of *justice* which Liebig vouchsafes to me, he has claims to any discoveries or experiments made in this protein investigation, let him

specify them. I do not speak of *repetitions* of words or numbers, but of what may be strictly termed a discovery. To *him* alone the honour must belong ; and even after he has appropriated whatever he can of my ideas, every thing must be again overthrown from bad humour, from a quarrelsome disposition, or from caprice, in order that he who has been robbed, and has not uttered one word about the theft, may be provoked to speak.

I know no more unfortunate state of existence. It is as remote from *truth* and *justice* as evil is from good.

## II. *The Properties of Protein.*

“ But,” says Liebig, “ *the properties of all these bodies that are one and the same*,—of fibrin, albumen, and casein,—are changed after they have been treated with potash. A mere solution in potash-ley, and re-precipitation by acetic acid, is therefore out of the question.” He could not obtain the precipitate of that *composition*, and with those *properties*, which I had assigned to the so-called protein.

And what are the properties that I have assigned to it? I have only stated, *that protein has all the properties which Berzelius mentions in his work as belonging to the class of substances which hold sulphur and phosphorus in combination, with the exception of those which are peculiar to the sulphur and phosphorus themselves* (Bulletin, 1838, pp. 109 and 110). For the sake of brevity I referred to these, and mentioned only two properties, viz., 1st, that of becoming purple by the action of hydrochloric acid ; and, 2d, of being precipitated by the prussiate of potash (Bulletin, 1838, p. 110). In thus referring to the work of Berzelius, it is clear that I meant only to call attention to the properties which fibrin, coagulated

albumen, casein, and vegetable albumen, have *in common*, and not those in which they *differ* from each other. In the "Natuur-en-Scheikundig Archief," Deel 6, p. 124, other properties besides the above are mentioned, which are, however, also common to fibrin and albumen, excepting those alone which are peculiar to the sulphur and phosphorus in these two bodies.

The properties which I assigned in 1838 to protein, from fibrin and albumen,—and since that time I have communicated nothing more as to its *properties*, but in regard to its *combinations* only—are the following: It has neither smell nor taste; is of a light yellow colour; easily pulverized; insoluble in water, alcohol, and ether; absorbs moisture from the air; swells in water, and becomes colourless. Heated upon platinum, it melts, burns with a flame, and leaves behind a charcoal which consumes completely, and much more quickly than that of fibrin and albumen. It is soluble in strong acetic acid, but previously becomes gelatinous. When to this solution prussiate of potash is added, a white precipitate appears. By hydrochloric acid it is changed in the same manner as fibrin. By strong sulphuric acid it is converted into a jelly, which contracts on the addition of water. With strong nitric acid it swells, becomes lemon-yellow, and, after being washed with water, orange-coloured. When boiled with dilute sulphuric acid, it becomes purple. It is soluble in caustic potash, and precipitated from the solution by acids; but on adding an excess of acetic acid, it is redissolved. When treated with a strong potash-ley, it disengages ammonia. By metallic salts it is thrown down from its solution in potash; and by basic acetate of lead, from that in acetic acid. A solution in potash does not blacken silver. (Natuur-en-Scheikundig Archief, 1838, p. 124.)

Now Liebig is at liberty to say which of these properties he has not found in protein. I have mentioned *no* others. If *he* can mention none, then he has once more proved that the question at issue is unconnected with protein.

It is possible that protein, obtained from different sources, may possess different properties. Of this I had then no experience. Nothing but malevolence can assert, that when prepared from fibrin and albumen, it could not have the properties that I have described, that is, *those common to the albuminous substances*.

An important point, however, remained as to the proportion of sulphur. Liebig could not obtain the protein free from sulphur, and upon that point also, I am requested to give a *very detailed* explanation. This sulphur, which, according to Liebig (see above, p. 30), is found in *exactly the same proportions* in coagulated vegetable albumen mixed with cellulose, in the fibrin of blood, in soluble vegetable and animal albumen, in legumin and casein; this sulphur he could not separate from these substances by treating them with potash.

With regard to this I could again refer to Scheerer, who specifies in all the other substances mentioned in vol. xl. of the Annalen,

Oxygen,  
Sulphur,

But in protein only, Oxygen.

This seems to shew, that Scheerer, although not having expressly stated it, has actually obtained that substance free from sulphur. As it was a point particularly to be ascertained, whether or not protein contained sulphur, it can hardly be supposed that Scheerer, working under the eye of Liebig, should not have looked



for sulphur. If Liebig at that time neglected to draw his attention to it, this is most worthy of remark. The fault is Liebig's, and not Scheerer's ; because Liebig has everywhere appropriated the honour of Scheerer's experiments.

But this point has occurred to him now, and even before, as I have perceived from his letters. He mentions (*Annalen*, January 1846, p. 133), that Dr Laszkowski, in the laboratory at Giessen, had been unable to separate the sulphur from casein, albumen, and fibrin, when the potash-ley had been kept boiling for several hours : when precipitated from the potash-ley, and even when fused with caustic potash, and neutralized by an acid, they still yielded sulphuretted hydrogen.

### III. *On Protein free from Sulphur.*

I come now to the most important fact—one which will perhaps contribute to our knowledge of the human heart—shewing how a thirst for fame may obscure—completely obscure—the knowledge of the very first elements of science in a man thoroughly conversant with them ;—or rather, how a thirst for fame may create in him the blind, but ardent conviction, that all men of science will neglect to employ its first principles just where they require them.

When sulphur is dissolved in potash, either by fusion or by boiling in water, then, as every tyro in chemistry knows, sulphuret of potassium is formed ; but, at the same time, the oxygen from the potash must combine with something else. He knows, further, that from four equivalents of sulphur ( $4\text{ S}$ ), and three of potash ( $3\text{ Ka O}$ ), there are produced two equivalents of sulphuret of potassium ( $2\text{ Ka S}$ ), and one of hyposulphite of potash ( $\text{S}^2\text{ O}^2\text{ Ka O}$ ) ; that sulphuret of

potassium (Ka S) exposed to the air, is converted into hyposulphite of potash ( $S^2 O^2 Ka O$ ); that when an excess of alkali is present, the hyposulphite of potash is converted into one equivalent of sulphite, and one of sulphate of potash ( $SO^2 Ka O$  and  $SO^3 Ka O$ ); and finally, that when some acid, for instance acetic acid, is added to hyposulphite of potash, sulphurous acid ( $SO^2$ ) is expelled, and sulphur precipitated.

Liebig, no doubt, teaches these things every year to his pupils; they cannot be passed over in any place where chemistry is taught.

Now, if a certain body,  $X (C^{40} H^{30} N^5 O^{12}) + S^*$  is dissolved in potash, so that the sulphur leaves the organic group, what will take place? This is a question which every one must ask of himself when examining these protein compounds. It is a question which Liebig has not presented to his own mind, and to which the knowledge—the elementary knowledge—of chemistry had given him no answer. Truly a remarkable phenomenon in science! To be engaged for years in the study of a subject which can be made intelligible to children, and at last to come forward with a *friendly* question; but beneath which show of friendship I very well knew what was concealed. Happy in having proved to the world, as he thought, that no such substance as protein existed—upon part of my work much discredit was thrown, and the ABYSS,—as he thought,—was not now far off!

How is it possible, that “a man, who speaks of forces in sulphur and selenium, who saw hydrogen disengaged, when hæmatine was treated with sulphuric acid, and hence concludes, that iron exists in hæmatine in the metallic state;” a man who, accordingly, “does not

\* I take no notice of the phosphorus, because, in the case in question, I can give no account of it that can be tested.

stand on the height of science," (thus Liebig writes in his letter of 29th May last)—that such a man is obliged to recall to Liebig's mind the properties of sulphuret of potassium and of hyposulphite of potash;—to point out these to him with emphasis, because, allowing his elementary knowledge to lie dormant, or leaving it purposely unemployed, he puts a seeming friendly question with an ABYSS in prospect. (The reader knows what Liebig means by ABYSS: It means an article in the *Annalen* from his pen! Whenever such an article appears, Liebig thinks, that the man against whom it is directed is morally dead, and that he need neither expect nor fear any farther influence from him upon that public which Liebig seeks to please).

Let us—however ignorant I may be—not leave unapplied our knowledge of sulphuret of potassium and the hyposulphites, but let us use it where it is necessary; that is, where an organic substance containing sulphur is dissolved in potash.

It would be needless for me to remind the reader, that when four equivalents of sulphur are dissolved in an excess of potash, the action of the air causes the rapid formation of two equivalents of hyposulphite of potash, and that, at the same time, two equivalents of sulphur are precipitated from this by an acid, being half of the sulphur that was originally used. When either fibrin, albumen, or casein, are treated with a weaker or stronger potash-ley at an *elevated temperature*, so as to make these substances dissolve, acetic acid is then added to the solution, a large quantity of sulphuretted hydrogen is disengaged.

Whence does this gas arise, if not from sulphur, which the potash has separated from the protein compound? The question, therefore, cannot be, whether the potash separates *any sulphur*, but whether it sepa-

rates *all*? That sulphur is separated from the white and yolk of an egg by very weak alkaline solutions, is familiar to every chemist.\*

In my former experiments, when I digested the substances at a *higher* temperature, I had never discovered a trace of sulphur, on heating the protein with potash upon a piece of silverfoil. In now repeating the same experiments, I found not a trace of sulphur in protein from albumen, on burning the organic substance with carbonate of potash and nitre.

In other products, prepared in a similar manner from albumen, fibrin, beef, and veal, I have sometimes obtained substances perfectly free from sulphur; while at others some sulphuric acid has appeared after the substances were burnt with nitre and carbonate of potash.

Has Liebig now any right to deny the existence of protein, because it may contain sulphur,—sulphur of which at one time he would not hear—which hitherto was of no consequence, but which may now be of use in enabling him to deny the existence both of protein (*Annalen*, January 1846) and of bi-oxide of protein.

The impartial man of science does not act in such a manner. In the *first* place, protein can be obtained, with the greatest ease, free from sulphuric acid and sulphur; but even although it could not be so obtained,—although the method of separating the latter were not yet known,—although Liebig's formula for protein  $C^{48} H^{36} N^6 O^{14}$  were completely unfounded—no one who has investigated Nature on this subject will dare to deny, that, in this long series of albuminous substances, there exists a peculiar body, by which we were enabled to connect them together in a class, ex-

\* The blackening of a silver spoon by a boiled egg is caused by this sulphur.—T.

tensive even before protein was known, but which, since its discovery, has been very much enlarged.

From whence comes now this *imponderable*, but yet *visible*, trace of sulphuric acid, which is obtained, not from *all*, but from *some* kinds of protein, by burning with nitre and carbonate of potash? Is it really sulphur? Is it possibly not sulphuric acid?

The first thought which forced itself upon my mind, was that of an *impurity*—arising either from part of the original substance, which, although dissolved in the alkali, had not been completely separated from the sulphur, or from sulphur itself, or from sulphuric, sulphurous, or hyposulphurous acid. In every case, it is *impurity*; for, I repeat it, that there is no difficulty in obtaining protein from all substances in which it is present, without *any trace* of sulphur or sulphuric acid.

But if it, perchance, should contain sulphuric acid, after combustion with nitre and carbonate of potash, in what amount is it? Is it less than was originally found in the substance employed? What, then, is the cause of that decrease? If the proportion of sulphur diminishes to one-half, one-fourth, or one-third, what is it, then, that has been obtained? Certainly not the original substance, for this contained the whole of the sulphur.

These are questions which the impartial man of science really desirous of finding the truth, and not of placing obstacles in the way of others, asks himself, and readily solves.

How is protein to be obtained free from sulphur? From albumen, for example, by the employment of a potash-ley of such strength, at such a temperature, and so long, that the sulphur is caused to leave the organic group. This commences even at the ordinary temperature, if a strong ley, containing one-tenth of the hydrate

of potash, has been used, but requires a higher temperature, if a weaker solution be employed. There is a fixed relation between the strength of the alkaline ley, the quantity of albumen dissolved by it, the temperature to which it is exposed, and the period during which the action is protracted. I shall, presently, treat of this more in detail, but must here mention a fifth condition, upon which the successful preparation of protein depends, viz., the influence of the air after the sulphur has been completely separated.\*

Under these circumstances the following action takes place. The sulphur of the albumen combines with potassium, and forms sulphuret of potassium; the oxygen of the potash goes to form hyposulphurous acid, which unites with the potash.

When now a solution of sulphuret of potassium is exposed to the air, it is again converted into hyposulphite of potash. By a protracted contact with the air, this salt becomes more highly oxidized; but if this contact is not long continued, and it remains wholly or partly in the liquid state, and then an acid is poured upon it, the hyposulphurous acid will be decomposed into sulphurous acid and sulphur,  $S^2O^2 = SO^2 + S$ . The sulphurous acid is expelled, the sulphur is necessarily precipitated and *mixed*, not *combined*, with the protein, which is at the same time thrown down. Now, as hyposulphite of potash is directly formed in the first instance, and a sufficient supply of oxygen will always obtain access to convert part of the sulphuret of potassium into the hyposulphite, it is natural, in every case

\* This and all other scientific parts of my writing is not intended for Liebig. I do not wish to receive from him any more of his justice; I am satisfied with what I have already received. The discoveries of another are not considered true, unless he himself derives honour from them.

where the hyposulphurous acid has not yet become more highly oxidized, that so much sulphur should be mixed with the protein, as always to form a precipitate with it. Hyposulphite of potash is constant in the air, but when an excess of alkali is present (as is the case here), it is converted into two equivalents of sulphite of potash ( $S O^2 K a \cdot O + K a O = 2 (S O^2 K a O)$ ), and subsequently into two equivalents of sulphate of potash,  $2 (S O^3 K a O)$ . Before this change has taken place, however, the half of the sulphur must fall along with the precipitated protein. It is well known, that hyposulphite of potash is produced from sulphuret of potassium on exposure to the air, and that this salt is also formed when sulphur is dissolved in potash.\*

Liebig ought not to have required me to draw his attention to matters of this kind; for they belong to the first elements of chemistry, in which he needs no instruction from me.

Since we are now upon the elements of chemistry, with which Liebig is better acquainted than I am,—and I have not a moment's hesitation in repeating this before the scientific world, because it is true,—I must make one other remark about the sulphuretted-hydrogen, which is disengaged upon adding acetic acid to the potash-ley, in which fibrin, albumen, or casein, are dissolved. I found it very easy to prevent this disengagement, though with Liebig it seems to have been otherwise. Whence arises this difference?

The reason is simply this: that I allow such operations a few days' time. The sulphuret of potassium

\* When sulphur is dissolved in potash alone, and acetic acid added, a precipitate of sulphur is always found, even when the potash is in large excess. This is derived from the hyposulphite of potash produced.  $(3 K a O + 4 S \text{ produce } S^2 O^2 K a O + 2 K a S.)$

has then been converted into the hyposulphite, and the latter into sulphite or sulphate of potash, and now the acetic acid can no longer expel any sulphuretted hydrogen. It is clear that Liebig, who constantly speaks of sulphuretted hydrogen, must have experimented quickly. If Liebig were open to advice, I should say to him, Allow these substances sufficient time, and you will separate the whole of the sulphur.

From what has been stated, it is evident, that protein containing sulphur, may be prepared from a compound of sulphur and protein, without any of the original substance remaining; for example, protein containing sulphur may be prepared from albumen, without any albumen being left. From the composition in the hundred parts, the sulphur may then be subtracted. In other words, if the albumen employed contain 1 per cent. of sulphur, and by dissolving it in potash and precipitating by acetic acid, we obtain a product containing 0.3 per cent. of sulphur, it is by no means necessary to assume that three-tenths of the precipitate still consist of albumen, or of some new compound of an organic substance with sulphur. This sulphur is merely derived from the hyposulphite of potash, and is thrown down by the acetic acid together with the protein. When it cannot be removed by a solvent, the albumen has either been treated with too weak a potash-ley, or at too low a temperature.

The sulphur therefore, of which Liebig speaks in the experiments of Dr Laskowski (p. 43 above), is only an admixture, and not a chemical combination. A potash-ley of moderate strength, after having been boiled with albumen for some hours in the air, contains no longer any organic substance combined with sulphur;—no such organic body is thrown down by acetic acid, it only contains an *admixture* of sulphur, derived from the decom-



position of the hyposulphite of potash, as Liebig might readily have understood from general chemical principles. By boiling, the access of air is prevented, the oxidation of the sulphuret of potassium, and the production of hyposulphite, sulphite and sulphate of potash, only takes place imperfectly, and the hyposulphite, which is directly formed, is but partially converted into sulphite or sulphate. \* The oxidation can only be completely effected by prolonged contact with the air. I repeat, these facts are mentioned in every chemical manual, and Liebig is well aware of them.

If protein, free from sulphur, is required to be rapidly prepared, a compound of sulphur and protein must be treated with moderately strong potash, at a temperature of about 140° Fahr., and the precipitate produced by Acetic acid digested not only with the usual series of solvents, but also with some other in which sulphur is soluble.

And now I naturally arrive at the consideration of a part of Dr Laskowski's criticism of the protein theory (See the end of this article). We are indebted to this chemist for a new method of quickly preparing protein. Liebig, who again employs Laskowski to contend for him, as he does so many young men who go to Giessen to acquire a little of his knowledge, has not said a word to him about the properties of sulphuret of potassium, and hyposulphite of potash, and has, on the contrary, directed him to boil—actually *to boil*—a solution of sulphuret of potassium and hyposulphite of potash, in order, by this process, to prevent the indication of sulphur by acetate of lead. Now this is a tedious and difficult method. The mere boiling of 10 milligrammes of flowers of sulphur alone in potash-ley until there is no longer a reaction upon acetate of lead, would be very troublesome; but to take 100 grains of a protein

compound which contains, for instance, 1 per cent. of sulphur, and to boil away this 1 grain of sulphur, would be tedious in the extreme. And what must, in the mean time, become of the organic substance ?

It was impossible for Dr Laskowski to carry out this long process, and therefore two substances were employed, the use of which is actually to be acknowledged as an important contribution to our knowledge of the methods of preparing protein. These substances were oxide of bismuth and silver. The addition of these substances to the solution did not take away the sulphur from the substance, for this was done already by the potash, and could not be effected by these bodies ; but they decomposed the sulphuret of potassium and the hyposulphite of potash. Thus, the desired object was at last obtained by Laskowski, and a liquid was prepared, from which acetic acid precipitated a flocky organic substance *free from sulphur* ; whilst another substance was held in solution, only differing from the former by its solubility in water (*Annalen*, Mai 1846, p. 158–160). The precipitate was analysed, but Laskowski himself attaches no value to this analysis.

A second time, therefore, protein has been prepared at Giessen ; *and thus the same paper which denies the existence of protein, actually confirms it*, for a careful examination will shew that the precipitate produced by acetic acid, and *free from sulphur*, is protein. But to say it is so, and it is not so, is precisely the master's method of reasoning. He says, none are right, and none are wrong ; you know a great deal, and you know nothing. He at last finds the substance which I have indicated, and then denies its presence.

A remarkable phenomenon indeed ! A substance free from sulphur cannot be obtained. It is said *to have no being—to exist merely on paper* (*Annalen*, Mai

1846, p. 148 and 164); and yet *a substance free from sulphur* is obtained (Ibidem, p. 159), even without a knowledge of the properties of sulphuret of potassium and hyposulphite of potash.

Remarkable phenomenon! Not only is *a precipitate free from sulphur* obtained, on adding acetic acid to a solution of albumen in potash, but *the same thing also is found which Van Laer discovered some years ago*, while passing a current of chlorine through a liquid, from which protein had been thrown down. A precipitate was obtained, the quantity of which was large, in proportion as less protein had been previously separated (Scheik. Onderzoek., Deel 1, p. 170), that second body, namely, which, identical in composition with the precipitate, but soluble in water, remained in the liquid obtained by Laskowski.\* These substances, free from sulphur, which at the same time *exist and have no existence*, were never thought worthy of analysis; it was merely said, "*There is no protein. I obtain, what you have mentioned; but what have you mentioned? Why, only certain substances; but what do they concern me? They cannot be what you represent them to be, although I may find them the same, identically the same, bodies: for the discovery was not first enunciated by me.*"

If this is not the way in which Liebig reasons, I do not understand the contents of the May Number of the Annalen 1846, p. 158-160, and p. 164. But in whatever way he may reason, I will henceforth hold to Dr Laskowski's statement, viz., "*that when albumen is treated with a potash-ley, two substances are produced free from sulphur, the nature of which is NEARLY THE SAME, —for Laskowski boiled the ley,—as that of the substance which I have called protein.*"

\* According to Laskowski, the latter is chiefly produced from casein. (Annalen, Mai 1846, p. 161.) See below.

I may detail this matter more distinctly. Dr Laskowski could not decompose the sulphuret of potassium and hyposulphite of potash by boiling; and he used oxide of bismuth or silver for the purpose of separating the sulphur, both of which substances remove the sulphur from a solution of flowers of sulphur in caustic potash so completely, that acetic acid does not cause the precipitation of any sulphur. The oxygen of the air would have done the same, if, after having heated the liquid, and thus separated the sulphur from the organic group, he had exposed the solution to the air at the ordinary temperature, until the sulphuret of potassium and the hyposulphite of potash were converted into sulphite or sulphate of potash.

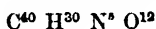
I repeat, therefore, *that silver or that oxide of bismuth have nothing to do with the removal of sulphur from the organic group, for this was already done.* If, therefore, Dr Laskowski had not employed oxide of bismuth or silver, but merely the oxygen of the air, he would have obtained the same products that he did.

And what has he *obtained*? By means of acetic acid he has thrown down from the potash-ley a precipitate, which was *free from sulphur*;—a flocky precipitate, insoluble in water, alcohol, &c.; or, in other words, the very substance which I have called *protein*.

Now, I ask, what ought to have been done to correspond with a criticism, in which protein is *deprived of existence*, and called a *substance upon paper*? After a flocky precipitate, *free from sulphur*, has at last been obtained by means of acetic acid—(I have never mentioned any other substance under the name of protein),—it should have been the duty of the criticiser carefully to examine this precipitate. This, however, was not done. He makes a *rude experimental analysis*, which he himself does not consider as correct. Is it al-

lowed to publish analyses, which are *not esteemed good by the experimenter himself*, in order to depreciate the labours of another?

The result will shew, that the *precipitate free from sulphur*, obtained by Dr Laskowski from the potash solution by means of acetic acid, if *duly prepared*, has no other composition than is represented by the formula



the proportion of carbon, which he found in the first instance, completely agreed with that in protein (C=75.12), viz.

Precipitate free from sulphur obtained by Dr Laskowski,	Protein.
C = 54.6	C = 55.02

By a correct analysis, the following result and no other will be obtained:—

$$\begin{aligned} \text{H} &= 6.8 \text{ to } 7.0 \\ \text{N} &= 15.6 \text{ to } 16.0 \end{aligned}$$

It is now in the power of every one to judge, whether the chemists that do not belong to Giessen are there treated justly or unjustly? Have I ever described as protein any other substance than *a precipitate free from sulphur, obtained by means of acetic acid*? When such a precipitate has at last been obtained, is it proper then to pass it over with mere experimental analyses? He who does so is, in my estimation, an unjust man, whose object is not truth.

Again, Laskowski has obtained from a solution of albumen in potash-ley, by means of acetic acid, a precipitate free from sulphur, which, according to an experimental analysis, contains

C	54.6
H	6.0
N	23.9
O	15.5

The question, therefore, now no longer is, whether

such a precipitate free from sulphur can be obtained, but what is its composition? This was determined by myself, Scheerer, Dumas, and Cahours, not by experimental analyses, but by others which I believe are correct, and found to be ( $C = 75.12$ ).

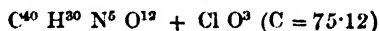
C	55.09
H	6.86
N	16.04
O	22.01

I would ask the reader what impression this kind of justice makes upon him? Is such conduct not a disgrace to our century?

I am, however, far from laying any charge against Dr Laskowski as yet (see the end of this article). As usual, Liebig, in the Number of his *Annalen* for January last, gave a preparatory account of the nature of Laskowski's communication, which was to appear in the May Number, in order that he (Liebig) might get the credit of it. Consequently, I now speak of Liebig, and willingly offer the hand of friendship to Laskowski. I here tender my kind thanks to this antagonist of protein, because he has once more proved to the world, that a *precipitate free from sulphur* can be obtained from albumen.

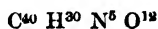
As regards the substance likewise free from sulphur, which remains in solution (p. 413 of the above *Annalen*), Van Lacer has analysed it, as it appears in combination with chlorine.

It is either protein or oxide of protein; for, according to the proportions of carbon and hydrogen, it is



Liebig, to whom I have regularly sent the *Scheikundige Onderzoekingen*, ought to have mentioned this to Laskowski, for it is there stated, Deel i. p. 170. The quantity which is obtained is larger, as the alkali employed

is stronger, or the temperature higher to which it is exposed, and, under the same circumstances, the quantity of protein precipitated is smaller. *This body, free from sulphur, soluble in water*, obtained from albumen and other protein compounds, proves the value of the empirical formula,



as much as *the precipitate free from sulphur*.

Honoured reader! tell me—Could I, by any possibility, have had a more useful antagonist than Laskowski, who completely confirms the point in question?

I consider Laskowski, then, as an honest man. Liebig has not wished any further mention to be made of these two bodies free from sulphur. Having come so far, it was necessary to stop, but every man of common sense must acknowledge, that there, where he has stopped, he ought to have commenced.

Chemists, who are acquainted with the nature of sulphuret of potassium and hyposulphite of potash, will oblige me exceedingly by again examining these two compounds. The fear of the man in Giessen will surely not be so great as to deter them from this undertaking.

But how did I formerly prepare protein? In the Bulletin de Neerland, 1838, which contained only short abstracts of treatises that appeared in the Netherlands, very little is mentioned about the manner in which I prepared it. At p. 109 I have said, "*Quand on traite la fibrine, l'albumine de l'œuf ou du serum par la potasse caustique très-faible, la matière se dissout entièrement. Par l'acide acétique on précipite une substance floconneuse, que j'ai lavé,*" &c. Not one word, therefore, is said concerning the *temperature* at which these substances have been dissolved in potash.

But this was only an abstract of a more detailed me-

moir on this subject. At p. 104 of the Bulletin, it is stated, "J'en donnerai un extrait dans ce Journal, tandis que je renvoie le Lecteur à l'Archief, tome 6, pour les détails, que je passerai pour le présent."

Among those details, it is mentioned, vol. vi., p. 119 of the *Natuur-en-Scheikundig Archief*, "*that fibrin and albumen were dissolved in potash at a temperature of about 140° F.*"

I think I have a right to require, that, if a man accuses me of having published accounts of substances which *he* also has once found—finds, but cannot now find again—and this is the meaning of what Liebig writes now, in the *Annalen* of January and May 1846,—that such a man should read what has been said upon the subject, not in an abstract, in which the reader is referred to the original paper, but in that original paper itself.

To Liebig that was unnecessary.

We read in the *Annalen*, January 1846, p. 132, "When fibrin, albumen, or casein, are, according to *Mulder's directions*, dissolved in potash-ley of moderate strength, and then neutralized with acetic acid, no protein free from sulphur, as *Mulder believes*, is precipitated. I have found, that when this solution is mixed with some lead-salt, it does not blacken it in the least. When the white precipitate obtained by acetic acid is washed and dissolved in a potash-ley, and then boiled, this liquid, when mixed with sugar of lead, becomes black as ink."

It is here said, that I *direct* and *believe*; and neither of these assertions is true. I have never *directed* fibrin and albumen—I have not spoken one word as yet of casein—to be dissolved at the ordinary temperature in potash, and then to precipitate; but I have said, that the solution must be effected at about 140° F. The rashness with which so frequently Liebig judges, is



here also the cause of his ascribing to me words which I have never uttered.

A man who can dissolve fibrin, albumen, or casein, in potash, at a temperature of about  $140^{\circ}$  F., and then says, "I have found that this solution, when mixed with sugar of lead, does not blacken in the least," states facts, of which I have asserted just the contrary.

I repeat once more: "I have prescribed, in my memoir on this subject, in the *Archief*, 1838, p. 119, the *employment of a temperature of about  $140^{\circ}$  F. for the preparation of the solution of fibrin and albumen*. Liebig should have either made the experiment in this manner, or not at all.\*

This part of Liebig's attack, therefore, falls to the ground. Fibrin, &c., dissolves in a weak ley at the ordinary temperature, without parting with sulphur. If not kept for a sufficient length of time at a temperature of the requisite degree, it only loses *part* of the sulphur; and the presence or absence of sulphur in the precipitate, is the test which indicates whether the protein is pure or not.† At a boiling temperature, the sulphur may be separated from the protein; but this is not sufficient either to convert the hyposulphite of potash into sulphite and sulphate, or to decompose the sulphuret of potassium. This is only effected by a longer contact with the air. I repeat, that, when the air has free access, the hyposulphite of potash in a few days becomes more highly oxidized, and after that the pre-

\* By about  $140^{\circ}$  F., I mean the temperature of a sand-bath. This *about* may have signified sometimes less, sometimes more, than  $140^{\circ}$ . I did not, at that time, understand the reason for employing this temperature as I now do. At all events, I said *about*  $140^{\circ}$  F., which certainly does not express any great accuracy.

† The temperature at which the various sulpho-protein compounds, in a potash-ley of a certain strength, begin to part with their sulphur, is very variable. Horn does it quite readily; albumen loses sulphur in a ley of  $\frac{1}{10}$  of caustic potash, even at the ordinary temperature.

cipitate contains not a trace of sulphur. The liquid should not be heated to boiling, because then, especially when the alkaline ley is too strong, the protein is decomposed.

This, therefore, has been my practice. I placed a quantity of potash-ley, with some protein compound in it, on the sand-bath, at a temperature of about  $140^{\circ}$  F., for albumen and fibrin. I candidly confess that I did not then understand, as I now do, either the value of a regulation of temperature, or of the degree of strength of the potash-ley, or of the time of action, or of the influence of the air. I candidly acknowledge, that I have merely put *aside for some days* albumen and fibrin, heated to *about*  $140^{\circ}$  F., more or less, not caring much about the circumstance, *except the time of action*.

My friend, Professor Schlossberger, who paid me a visit in December last, and therefore before the last January Number of the *Annalen* had appeared, can testify, that he has seen, with me, albumen in potash-ley, placed on the outside of a vapour-bath, which had a temperature in the interior of  $200^{\circ}$  F., but on the exterior of  $140^{\circ}$ — $176^{\circ}$  F., and left there for some days. From this solution he has himself precipitated protein, but did not farther examine it; and every one who has ever visited my laboratory, and has either himself prepared protein, or seen it made, can testify, that the substances were left upon the sand or vapour-bath for a number of days, in a moderately strong potash-ley.

I therefore lay no claim to peculiar acuteness in the discovery of protein free from sulphur; I must, on the contrary, accuse myself for not having better studied all the circumstances attending its production. But I can the more positively declare, *that I have not found a trace of sulphur in the substances, which I threw down*

*by acetic acid from a potash-ley, placed upon a sand-bath, when I employed fibrin or albumen.*

What I have now to add to the method of preparing protein is as follows: Take a potash-ley, containing  $\frac{1}{10}$  of hydrate of potash, mix it with coagulated albumen, previously washed with water, so as to cause it to dissolve speedily, and let the whole remain upon the sand-bath at a temperature of  $140^{\circ}$ — $176^{\circ}$  F., until the reaction of sulphur no longer increases. Let the liquid remain exposed to the air in a large basin, at the ordinary temperature, stirring it frequently, to oxidize the sulphuret of potassium and hyposulphite of potash. Then precipitate with acetic acid,\* and repeat the same operation with the same substance, should the precipitate still contain sulphur. Wash it with warm water, digest it with alcohol and ether, and do not consider it pure if any sulphur or sulphuric acid be found in it. When the potash-ley is stronger, the protein free from sulphur is formed more readily, but in such case, the temperature and time should be regulated accordingly.

Recently, however, I have endeavoured to discover more certain methods. In employing these methods, it has appeared, that the alkaline ley, even when weak, should not be boiled; that at  $176^{\circ}$  F. at the utmost, and in a ley containing  $\frac{1}{10}$  of dry caustic potash, a complete separation of the sulphur takes place in an hour's time; that is to say, that for the coagulated albumen of four eggs there should be taken 50 grains of potash to 500 grains of water; that then only a small quantity of de-sulphuretted precipitate is obtained, but, on the contrary, a great deal of a soluble substance, free from sulphur, which can be precipitated with chlorine.

\* The smell which is here emitted does not arise from sulphuretted-hydrogen; this gas ought now no longer to be disengaged.

The white of 8 eggs, mixed with 20, 30, or 40 grains of potash, and 1000 grains of water, being exposed for five hours to a temperature of  $203^{\circ}$  F.,—that is, nearly the boiling point,—yields almost no precipitate of protein, but a very large quantity of a soluble substance free from sulphur. The solution, therefore, in both cases, was too strong, or the temperature too high—perhaps both conditions had an influence.

The white of 12 eggs, mixed with 40, 20, 10, or 5 grains of potash, and 2000 grains of water, exposed for one hour to a temperature of  $203^{\circ}$  F.—again under the boiling point—in each case produced, with acetate of lead, a precipitate, which, from the three first, was as black as ink, and all in the same degree—from the last it was only brown-coloured;  $\frac{1}{400}$  of potash therefore is too weak, but  $\frac{1}{200}$  strong enough to accomplish the same in one hour, as is done with  $\frac{1}{20}$  of potash. The ley of  $\frac{1}{400}$  having been kept at that temperature two hours longer than the former, produced an equally dark colour with the lead-salt, as in the three former cases.

A little of the three first solutions, when tested with acetic acid, yielded abundant precipitates. The solutions were exposed to the air at the ordinary temperature, and frequently stirred, to enable the oxygen of the air to penetrate them. The reaction with acetate of lead gradually disappeared, and after this was no longer manifested, the liquid was exposed to the air four days longer, frequently stirred, and finally filtered and precipitated.

When this method is employed, a precipitate will be obtained, which, when boiled with a perfectly saturated potash ley, does not produce the slightest change of colour with acetate of lead.\*

But we possess more delicate reagents than acetate of lead, poured drop by drop into a solution which

has been boiled in a strong alkaline ley. A portion of the substance, in a strong ley, must be heated on a thin piece of silver, and allowed to remain thereon in the remainder of the potash-ley. If, after having remained there an hour, no change of colour is perceived on the silver, the substance is free from sulphur. Protein, which after being long boiled in a strong solution of potash, and then mixed with acetate of lead, gave no trace of sulphuret of lead, still yielded a distinct brownish spot upon silver, when it had been acted upon by potash.

If any chemist still feel inclined to consider this body as albumen, let him burn it with nitre and carbonate of potash, and after dissolving it in weak nitric acid, add chloride of barium. He will find no trace of sulphate of baryta, because this salt is not sufficiently insoluble to indicate the minute quantity of sulphur that may still be present.

Such a body, in the ordinary acceptation of the term, as used by every chemist, may be said to be free from sulphur. Every one who has prepared protein a few times, and has attempted to do it with accuracy, will easily succeed in obtaining a substance which does not produce the slightest discoloration of a silver plate. It must then again be digested in potash at a low temperature and re-precipitated; for, generally, a trace of sulphur is still mixed with it, derived from the hyposulphite of potash which had not been completely decomposed. Dr Laskowski found a trace of sulphur (*Annalen*, Mai 1846, p. 162) in all the products which he obtained. "The quantity of the latter, viz., sulphuretted-hydrogen was, however, so *exceedingly minute*, that I do not venture to <sup>assert</sup> that the sulphur here discovered did not arise from the admixture of some foreign substance." It is impossible to speak more

plainly than Laskowski does here. But this is not allowed to be called *my* protein; its discovery belongs to Giessen, and it is naturally immaterial to me how it may be received. I do not contend in defence of my discoveries, but I speak of Liebig's attempts to depreciate those of others. It is not I, therefore, who have obtained protein free from sulphur; this, according to his account, has first been accomplished in Giessen. And at this Liebig feels himself quite elated.

But did not Liebig, who makes it appear now in his *Annalen*, as if I had treated fibrin, albumen (and casein), with potash, at the ordinary temperature, and had obtained protein in this way,—did he not know before, that I had employed for this purpose *an elevated temperature*? Is not his present object, therefore, a wilful perversion of truth? “*As Mulder directs, as Mulder believes*” (these are his words).

Will the reader be so good as to refer to the article “Blood,” in “*Poggendorff und Liebig's Handwörterbuch*, vol. i., p. 890.” There he will find the following words written by Liebig:—“That fibrin or albumen must be treated with a moderately strong potash-ley, at 122° F., and that then the addition of acetic acid produces a precipitate of a substance completely free from sulphur and phosphorus, having the other elements present in the same proportion as in fibrin and albumen. The sulphur and phosphorus have been taken away, and the other elements have remained in combination. When the potash-ley is neutralized, a disengagement of sulphuretted-hydrogen is perceived; and after the precipitate has been removed from the liquid, the latter is found to contain a certain quantity of an *alkaline phosphate*.” So Liebig himself spoke in 1842. According to him, therefore, protein is prepared at 122° F.; according to me, at *about* 140° F.

We read, further, in the same book, p. 892, again by the same author, "the gelatinous (?) precipitate obtained by dissolving fibrin and albumen in a *heated* (erhizter) potash-ley, and afterwards supersaturating with acetic acid, dries into a *white* or yellowish-white mass, which can easily be powdered. Prepared from either substance,—fibrin or albumen,—it shews the *same character, and all its other properties are completely the same.*"

Further on, again (p. 893), we read:—"According to this," viz., the conformity between the results of Scheerer and myself, "we may consider it as perfectly certain, that fibrin and albumen, as regards the proportion of their organic elements, *are identical in composition.* Protein, prepared according to Mulder's prescription, contains in the 100 parts, by the

Analyses of Dr Scheerer :—

Protein from Albumen.	From Fibrin.
C 55.160	54.848
H 7.055	6.959
N 16.216	15.876
O 21.569	22.317"

Now, in the first place, I reason, in the spirit of Liebig, thus:—fibrin is identical with albumen, protein agrees in every respect with fibrin and albumen; protein, therefore, is identical with fibrin and albumen.

That was in 1842. But in 1846 I am desired to state, with full details, the mode in which this body should be prepared, although he has seen it prepared formerly by *himself* and Scheerer, and now by Laskowski.

But,—and this is of no less importance,—who ever spoke in 1842 of 122° F., and of heated *potash-ley* (erhizter Kalilauge)? I never mentioned 122° F., but *about* 140° F. Consequently, neither the words

nor the experiments to which Liebig referred in 1842 are *mine*, for in 1842 I did not know protein as a *white* substance, neither do I know it as such in 1846. It is quite certain, that Liebig speaks here of his own experiments, *as he writes about a substance altogether free from sulphur and phosphorus.*

Liebig ought, therefore, to render an account of *his own errors*, if any errors have been committed, instead of charging *me* with them; I am, at least, not inclined to submit to such a substitution. If Liebig had asked before what he now requires of me, it would have been my duty to answer; but now having spoken of 122° F., and of *white protein*,—now having himself described a method of preparing *protein free from sulphur*, having *the same properties*, and *the same composition*, as that which I obtained, it is for himself to defend what he has published as *his own work*.

It appears, however, from his words in the *Handwörterbuch*, quoted before, that Liebig either knew or supposed in 1842, that I had applied *heat*, and, therefore, it is not in accordance with good faith to make it appear now as if I had not done this, but had applied the *ordinary temperature*. It is impossible for any one to believe that Liebig could have forgotten in 1846, what he had written in 1842, on the same subject upon which he now throws doubts. In his *Thierchemie* (Animal Chemistry), 1842, p. 109, he again says: "In every case, the organic elements of the substances mentioned arrange themselves in the same manner, when they are brought into contact with caustic potash at an *elevated* temperature,"—a sentence which exactly expresses what I wrote in 1838; for *about 140° F.* means an elevated temperature.

I would, therefore, conclude this part of my subject,



by repeating *as Mulder does not direct, as Mulder does not believe*, and by observing that Liebig has purposely here told an untruth, simply with the view of complicating the protein question. My original memoir, in which I speak of *about 140° F.*, was actually read by him at the time of its publication; and now he endeavours to make it appear as if I had applied the ordinary temperature.

#### IV. Of Legumin.

I feel it necessary here to correct an error which I have committed in mentioning the experiment of Rochleder upon legumin. (The Chemistry of Veget. and Anim. Physiology, p. 297.) I had overlooked the fact (Annalen, vol. xlv., p. 160), *that Rochleder dissolved his legumin in a strong potash-ley without the aid of heat*; this was lately called to my remembrance on the occasion of Van Laer's experiments upon legumin. I, therefore, correct this error at once. Rochleder treated legumin with potash *at the ordinary temperature*; this I had misunderstood in his paper. But does this prove that *I* have not formerly applied a *heat of about 140° F.*, when treating these substances? Does this falsify what I published in 1838, and what Liebig himself, in 1842, copied in several places? I must speak distinctly; have I applied *no heat*, because I overlooked in Rochleder's paper, that he applied only *the ordinary temperature*? If any involuntary mistake should cause such a conclusion, this would become a sad, a dangerous precedent. All Liebig's works thus overflow with unparalleled mutilation of truth. Ought he not therefore to tremble when he takes up the pen?

It is a question to be investigated, whether or not

legumin contains sulphur, and if it does, how much? Liebig cannot mean, however, that he has prepared legumin in the manner mentioned by him in the January Number of the *Annalen*, 1846, p. 182. Whilst Rochleder only added a *few drops* of ammonia to the water with which the bean-meal was mixed, and threw down from this water the legumin, by means of acetic acid (*Annalen*, vol. xlv., p. 157), Liebig mixed peas-meal with *ammoniacal water*, and from this water, precipitated by acetic acid a mixture of *legumin* and *coagulated vegetable albumen*, the latter of which was rendered soluble by the ammoniacal water. Liebig knows very well, that the so-called coagulated albumen is soluble in ammonia, and that it is impossible by his method to prepare from peas-meal legumin free from vegetable albumen. Can it be, that Liebig is not aware of the presence of albumen in almonds and peas, and of the solubility of that albumen in ammonia? I cannot believe this. But Liebig must also then have known that he spoke of a *mixture of legumin and albumen*.\*

According to him, "its composition does not differ from that of the other nitrogenous vegetable substances

\* I directed pease-meal to be mixed with water at the ordinary temperature of a warm summer day, and digested it for some hours at a temperature of 95° F. The liquid was then filtered, first through cloth, and then through paper. To the perfectly clear liquid, acetic acid was added; the white precipitate was duly washed with water containing a little acetic acid, and then treated with alcohol. This precipitate I call *legumin*.

When the acid liquid is boiled after filtration, a large quantity of a second precipitate is produced. When this is separated by filtration, and carbonate of ammonia added to the liquid, a large quantity of a third precipitate appears. When, at last, the same peas-meal is digested in ammoniacal water, filtered through paper, and acetic acid added, a large quantity of a fourth white precipitate is obtained.

The first product is legumin; the second and third are probably soluble, and the fourth certainly insoluble vegetable albumen.

containing sulphur, which follows from the simple fact, that peas (?) contain all that is necessary to keep up the formation of blood, and through this to sustain animal life." (Annalen, Jan. 1846, p. 133.) In this way Liebig reasons; and we ought, therefore, never to enter with him upon the consideration of scientific questions, for he does not reason soundly, when life and vital functions are the subjects.

*Peas* contain everything; consequently, *one* of their constituents contains sulphur! Is he in earnest, or how is this to be taken?

Is the substance prepared by Rochleder's method,—viz., by dissolving legumin (free from albumen) in potash,—protein, or something else? Van Laer will soon publish his investigations on this subject. At present, I merely confine myself to the remark, *that it ought not to be called casein*, the less so, because animal casein is a complex body, a mixture of substances which have not yet been discovered in legumin. Whoever calls legumin *casein*, has studied neither of them. Whoever persists in asserting that they agree so perfectly with each other, as to be entitled to one and the same name, is determined not to seek for truth.

#### V. *Of Protein with Sulphur.*

By the use of a weak alkaline ley, by too low a temperature, or too short a period of exposure to the action of potash, no pure protein (that is, *free from sulphur*) can be expected from the protein compounds. A mixture of substances is obtained, part of which have lost, and part retain, their sulphur.

It is of some importance to inquire, what is the composition of these mixtures? This inquiry may lead to

an increase of our knowledge of the composition of protein itself; for, should it appear that the composition of that mixture is no other than what arises from a more or less complete separation of the sulphur (and phosphorus?), then the composition of protein will be established anew. If, for instance, albumen, partly deprived of its sulphur, be found to have a composition intermediate between albumen that has lost the *whole* of its sulphur, and albumen that has lost none, then no other conclusion can be drawn, than that the body which is free from sulphur must have the composition of albumen *minus* sulphur.

The quantity of sulphur (and phosphorus) that is present in albumen, casein, &c., is so small, that a partial separation of the sulphur cannot have much influence on the proportions of carbon, hydrogen, nitrogen, and oxygen; but the proof, which is afforded of the composition of protein by ultimate analysis, is so much the more complete. If, for instance, protein were a body totally different from albumen *minus* sulphur and phosphorus, then a mixture of albumen and protein would not give any indication of the composition of the latter.

The investigation of the following substances, all of which contain a certain quantity of sulphur, has led to the discovery of an additional peculiarity in protein. It may be obtained under two different forms, and this I have now to add to its history. When either a strong alkaline ley,—for instance, one containing  $\frac{1}{2}\%$  of dry caustic potash,—or a high temperature is employed to dissolve the protein compounds, acetic acid precipitates protein in an anhydrous state. In some cases this is deposited on the sides of the vessel, as a substance more or less coloured, sometimes even dark, which is at first flocky, but afterwards, while still moist, viscid and resinous. When dried at 266° F., it is anhydrous

protein. In this state I obtained it in my former experiments; from hair it is always extracted in this form. Dr Van Laer will be able to declare, that as he obtains it from hair, it always answers Laskowski's description. In this form, the quantity obtained is comparatively small. If the atomic weight of carbon be taken = 76.437, its composition is always according to the formula  $C^{40} H^{31} N^5 O^{12}$ ; but when = 75.12, the number of equivalents of hydrogen is only 30, and therefore the formula then becomes  $C^{40} H^{30} N^5 O^{12}$ , as I stated *already two years ago*, at page 294 of my work on "The Chemistry of Vegetable and Animal Physiology." I think it unnecessary to adduce all my former results, which accord with the following calculation. When C is = 75.12, the formula gives

Atoms.	Calculated.	
C 40	55.09	
H 30	6.86	
N 5	76.04	
O 12	22.01	Equiv. = 5454.2

The formulæ for the substances, which I have called bi-oxide and tri-oxide of protein, must therefore undergo a similar modification.

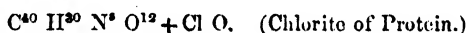
Thus the whole formula of protein may require to be modified, in consequence of the change in the equivalent weights of both carbon and nitrogen. That of the former was assumed to be 76.437, and of the latter 177.04, when I fixed the formula  $C^{40} H^{31} N^5 O^{12}$ . Now carbon is = 75.12, and nitrogen = 175.8, or 175.

The change of carbon alone produces a decrease of  $40 \times 1.317$ , which has an important influence on the composition. But as the means we possess for controlling the analysis of this protein are not so complete as those for uric and nitro-benzoic acids, I consider it at present superfluous to enter into an argument on this subject.

It might perhaps be thought better to have no formula at all? But why, then, has Liebig given formulæ for the vegetable alkalies? Of these the composition is also far from being known, and yet formulæ have been constructed for them. Why did Liebig himself give a formula of his own for protein?

I believe that my formula for protein has no more value than that for one of the vegetable alkalies, and if any one is able to correct it, he may freely do so. I shall be the first to hail it with pleasure.

But if the formula is at present still capable of defence, I am prepared to defend it upon the ground of the composition of the following substance alone,



It ought not therefore to be assailed without mercy, merely because it is offensive to Liebig. It is not *truth* to assume without foundation the formula  $\text{C}^{48} \text{H}^{36} \text{N}^6 \text{O}^{14}$ , whilst with chlorous acid ( $\text{Cl O}^3$ ) it gives in the chlorite,  $\text{C}^{40} \text{H}^{30} \text{N}^6 \text{O}^{12}$ . The man who seeks truth, should be above the paltry vanity of desiring to read his own formula in preference to that of another. For my part I shall willingly assume the formula  $\text{C}^{48} \text{H}^{36} \text{N}^6 \text{O}^{14}$  from the moment when good reasons are assigned for it.

It is remarkable that it should be considered improper to look for an equivalent weight of protein,—that it should have none,—that seeking for it should be iatro-chemistry! How much has Liebig fought, spoken, and written against it? This is because it was not discovered by himself. A formula is granted to bile, which is well known to consist of a variety of substances. Bile has an equivalent weight, and this although another has shewn that it is a mixture, and *cannot*, therefore, have an equivalent weight. Bile *must* have it, and *shall* have it. “*I will it,*” says Liebig.

Biline, . . . . .	} Are equal to C <sup>44</sup> H <sup>36</sup> N O <sup>13</sup> after deduction of the ash.
Fellinic Acid, . . . . .	
Cholinic Acid, . . . . .	
Choleic Acid, . . . . .	
Taurine, &c., with . . . . .	
Chloride of Sodium, Phosphates, Sulphates of Soda, &c., . . . . .	

Turnips, exhausted by boiling, have the formula C<sup>26</sup> H<sup>22</sup> O<sup>22</sup>! And yet none, according to Liebig, should be allowed to the independent organic group of the albuminous bodies! This cannot be called sound reasoning. The identical organ, which says,—the precipitate obtained by adding carbonate of ammonia to a solution of fibrin in hydrochloric acid, contains a trace of phosphate of lime, consequently this body ought not to have an equivalent number (Liebig's *Annalen*, January 1846, p. 131),—this identical organ, I say, remains silent when called upon to judge of its own idea of subtracting 3·5 per cent. of common salt from bile! This cannot be correct. In the moral world it would be called “seeing a mote in the eye of another, but overlooking the beam in one's own.”

What is the meaning of this, or how it arises, I know not; I will therefore give it no harsher name than that of an infirmity.

I repeat once more :—my formula for protein is no better founded than that of every other substance, *the constitution* of which is not well known, and the products of whose decomposition do not account accurately for every equivalent of carbon, hydrogen, nitrogen, and oxygen, that it contains. On the contrary, as protein is a substance having a very high equivalent weight, I think it quite possible that we shall yet obtain a new insight into its composition.

But is this a reason for calling the *present formula* false? It rests on the best information which we at

present possess. There are at present some grounds for the formula  $C^{40} H^{30} N^5 O^{12}$ , but none for any other. These grounds ought to be tested; they should either be confirmed by other proofs, or found insufficient, and rejected.

Again, I defend it, as I have said, on account of the composition of the chlorite of protein. If, in the investigation of such bodies, no more indulgence is granted in the search after a true and constant formula, than in the examination of the cyanogen compounds,—then the nature of chemical investigation is not understood, or what is required by justice is not granted.

Elaic acid has several times been the subject of investigation by very experienced men, and yet Gottlieb has recently shewn that they were all in error. The former investigations, nevertheless, *paved* the way for Gottlieb, and no one can call them unworthy. Whoever requires that I should reveal the whole truth at once in every examination of new substances, such as protein, would force me to bid farewell to science.

Where a weak alkaline solution, containing  $\frac{1}{100}$  of caustic potash, and a temperature of  $140^{\circ}$ – $170^{\circ}$  F. are applied, many, though not all protein compounds, are dissolved within twenty-four hours, and the solution is nearly colourless. If this liquid has not been long enough exposed to the air, the addition of acetic acid causes a disengagement of sulphuretted-hydrogen, and so abundant a precipitate is produced that great part of the substance employed is recovered. I say great part, for however weak the potash-ley may be, some of the substance is always decomposed. It would be erroneous to conclude from this, that protein does not pre-exist in such organic substances, as albumen. For when protein is dissolved in an alkaline liquid by



the aid of heat, ammonia is disengaged, and only part of the protein used is precipitated by acetic acid. If this precipitate be again dissolved in alkali by the aid of heat, and again thrown down by acetic acid, the quantity obtained is less than before, and thus, after repeated solutions and precipitations, the protein will at last entirely disappear. Whoever, therefore, denies that protein pre-exists in albumen, on the ground that only part of it is thrown down from the potash solution by acetic acid, and that ammonia is disengaged during its solution, ought also to deny that protein exists in protein, and even, that he had originally used albumen, because this is at last completely decomposed. Protein is a substance which is very liable to decomposition; it cannot be dissolved in an alkali without being at the same time partially decomposed. We find similar substances in tannic acid under the influence of alkalies, in the neutral fats when in contact with ammonia, and in several other substances. Van Laer has, however, proved long ago (Scheikundige Onderzoekingen, Deel I., p. 170), that even on the addition of hydrochloric acid to a solution of albumen in potash, the whole of the protein is not thrown down, and that on passing a current of chlorine through the liquid, after separation of the precipitate, chlorite of protein is produced.—See p. 58, *supra*.

By a low temperature, therefore, and a very weak alkali, we not only obtain the largest quantity of protein, from albumen for instance, but we obtain it also in a form, differing from that in which it appears on applying more heat and a stronger alkaline solution. By the first method, it may be obtained white as powdered chalk, and perfectly pure. It is thrown down from the solution by acetic acid, and appears as an abundant flocky precipitate which does not adhere to

the glass. It is washed first with cold and then with warm water, and while still moist is digested with ether, boiled with alcohol, and dried in the air.

When prepared from albumen in this manner, it is combined with sulphur, and yet it is no longer albumen; it *contains not a trace of phosphorus, and hardly a trace of incombustible residue*. It is as pure as under the circumstances could be expected. Its chief properties are the same as those I have described before, but it differs from the other kind of protein by containing one equivalent of water. This is the hydrate of protein.

An analysis of this kind of protein from albumen gave the following results (the quantity of sulphur in it caused a trace on a silver plate, but amounted to no more than 0.1 or 0.2 per cent.)\*

$$\begin{array}{l} \text{Phosphorus} = 0 \\ \text{Ash} = \frac{1}{2} \text{ per cent.} \end{array}$$

I. 0.554 gave 1.089 grains of carbonic acid, and 0.348 of water.

0.5875 gave M. Voelcker, of nitrogen—

42 cub. cent. before the exp. at 75° F., and 768 millim. barom. pressure,

117 cub. cent. after the exp. at 76½° F., and 767.5 millim.

II. 0.675 gave M. Voelcker—

1.323 of carb. acid, and 0.428 grains of water.

0.560 gave of nitrogen—

43 cub. cent. before the exp. at 70° F. and 768 millim.

114 cub. cent. after the exp. at 63° F. and 767 millim.

These gave, assuming the equivalent weight of carbon to be 75.12,—

	Found.		Atoms.	Calculated.
	I.	II.		
C	53.71	53.70	50	53.98
H	6.98	7.09	31	6.93
N	15.04	15.50	5	15.73
O	24.37	23.91	13	23.36 equiv. 5566.7

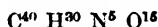
Differences, such as exist in protein, are found in seven-

\* See the proportion of sulphur in albumen, *infra*.

ral other substances. Without adverting to lactic acid and other bodies, I shall only mention here tri-oxide of protein, which, when in the soluble state, is represented by the formula,—



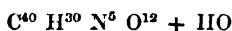
Whilst in the insoluble state it is



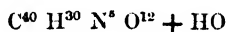
Van Laer obtained it in the latter form from the chlorite prepared from hair (Scheik. Orderz., Deel I., p. 161).

Bi-oxide of protein also occurs in two different forms, and perhaps in others besides.

The hydrate of protein,



is no doubt the form under which protein exists in several of its compounds. Now that this has been found (and before this there was unquestionably a blank in the history of protein), the compounds of protein will probably have to be re-calculated after the formula ( $C = 75.12$ ),—



Anhydrous protein may be prepared from fibrin, by means of a strong alkaline solution; but with a weak solution I have not been able to obtain it. Neither have I yet succeeded in separating the hydrate of protein from casein. By applying a weak alkaline ley at the temperature of digestion, and subsequently adding acetic acid, I obtained a large quantity of perfectly white anhydrous protein. After digesting this in warm water, and then burning with nitre and carbonate of potash, only a trace of sulphuric acid could be detected in it. In warm water it became soft and tough, differing in these respects from hydrate of protein, as obtained from albumen. Before I precipitated the protein, I left the potash-ley in contact with the casein, at an

elevated temperature, until the liquid, mixed with acetic acid, no longer blackened upon the addition of acetate of lead. The casein had been prepared by heating milk with acetic acid, washing the curd with water, and subsequently digesting it in alcohol and ether. The ley, employed for its solution, was heated to  $122^{\circ}$  F., and contained  $\frac{2}{3}$  of caustic potash.

0.381 left 0.002 of ash.\*

From 0.478 M. Voelcker obtained 0.9525 carbonic acid, and 0.302 water.

0.403 gave 0.810 carb. acid, and 0.257 water.

1.0375 gave of nitrogen—

before the exp. 53 cub. cent. at  $75^{\circ}$  F. and 759 millim.

after the exp. 189 cub. cent. at  $70^{\circ}$  F. and 759 millim.

C = 75.12,—

	Found.		Atoms.	Calculated.
C	54.75	55.15	40	55.09
H	7.05	7.12	30	6.86
N	15.77		5	16.04
O	22.43		12	22.01

By this result, I have the pleasure of confirming what Dumas and Cahours have stated. I had never before analysed protein from casein, but Dumas and Cahours have done so: they found (C = 75)

C	54.32
H	7.09
N	15.94
O	22.65†

\* The weights in all the analyses are grammes.

† After the protein from casein has been precipitated by acetic acid from the alkaline solution, and this acid has been added in excess, the additions of neutral acetate of lead produces a large precipitate in the clear liquid. This precipitate seems to contain hydrate of protein; at least the proportion of carbon and hydrogen were found to be

C	53.64	C = 75.12
H	6.90	

It was, however, mixed with an excess of phosphate of lead which I have deducted from it. We, therefore, require further investigations on this subject; but it is worthy of remark, that cheese possesses this property in

I must repeat here, that neither the substance from albumen, nor that from casein, were free from sulphur, of which they contained perceptible traces. Yet they had lost sulphur under the combined influence of the alkali and heat. They have further been prepared, with the precautions described at p. 65, and the solutions were deprived of sulphuret of potassium and hyposulphite of potash, by being left in contact with the air for a protracted period.

I consider neither of these precipitates to be *protein*, because they contain traces of sulphur. But although they are mixtures of much protein with a small quantity of the original substances employed, yet their composition does not agree with any other formula than that by which protein has been expressed. Should that expression of their constitution be objected to, therefore, because the substances were not *completely* free from sulphur? I still conclude that when albumen and casein are dissolved in a solution of potash by the aid of heat, and with the separation of sulphur, the addition of acetic acid produces a precipitate, the composition of which does not differ from that of protein. Were the latter substance so very accidental a product in the process of decomposition, the precipitates before described could not have given the results I have represented.

It is probable, therefore, that if the protein formerly prepared by Liebig, Scheerer, Dumas, Cahours, and myself, contained traces of sulphur mixed with it,—as may, for instance, have been the case with my vegetable albumen (Bulletin, 1838, p. 111), which, as

common with the white of eggs (parate the whole of the protein left is much greater than can be precipitated protein. Protein may a soluble form.

I now suspect, was not deprived of all its sulphur at the temperature of  $88^{\circ}$  to  $104^{\circ}$  F.,—still it could not have been perceived in the ultimate analysis.

I conclude then, from this, that the composition of albumen and casein, although only *partially* freed from sulphur, does not deviate from that of protein, but rather approaches to it; and, consequently, that albumen and casein are for the present to be regarded as consisting of protein with sulphur.

I say *at present*, for I have never ventured to attach a higher degree of certainty to this idea. I think it very possible that albumen, for example, is a combination of  $C^n N^m S$  with  $C^r H^s N^o O^q$  or with two or three groups, and that we shall still discover some method not merely of *separating all the sulphur* from it, but of separating this sulphuretted group from the rest. Now, should this be effected, protein will either cease to be represented as it is now, by  $C^{40} H^{30} N^5 O^{12}$ , or albumen will receive another name. But until an ultimate analysis yields something else than  $C^{40} H^{30} N^5 O^{12}$  with sulphur and phosphorus, this empirical expression is equally correct with that of cane sugar,  $C^{12} H^9 O^9$ , which is, in my estimation, neither more comprehensible nor scientific than the formula  $C^{40} H^{30} N^5 O^{12}$ .

From the analyses of the mixture here mentioned, I still therefore assume the same empirical formula for protein free from sulphur to which I have always adhered; and it appears, that all the analyses of albumen, &c., are to be considered as corroborations of the formula itself, provided we subtract from them the sulphur and phosphorus.

## VI. *Of the several Oxides of Protein.*

It will not be inappropriate to examine more closely

the substances that are derived from protein, especially those which I have called oxides of protein, a name which likewise offends Liebig (Annalen, January 1846).

If it be thought desirable to designate these substances by different names, they certainly deserve them; but for the present we have names not altogether inappropriate for the following bodies ( $C=75.12$ ):—

1.  $C^{40} H^{30} N^5 O^{12}$  anhydrous protein.
2.  $C^{40} H^{30} N^5 O^{12} + H O$  hydrate of protein.
3.  $C^{40} H^{30} N^4 O^{13}$  anhydrous protoxide of protein.
4.  $C^{40} H^{30} N^5 O^{13} + H O$  hydrate of protoxide of protein.
5.  $C^{40} H^{30} N^3 O^{14}$  anhydrous bi-oxide of protein.
6.  $C^{40} H^{30} N^4 O^{14} + H O$  hydrate of bi-oxide of protein.
7.  $C^{40} H^{30} N^3 O^{15}$  anhydrous tri-oxide of protein.
8.  $C^{40} H^{30} N^3 O^{15} + H O$  hydrate of tri-oxide of protein.

The *first* body is obtained from fibrin, albumen, casein, vegetable albumen, hair, and a great many other substances (Liebig obtained it also from horn, and Scheerer from the crystalline lens), by dissolving them in a tolerably strong solution of potash, and applying an elevated temperature for a short time. It is thrown down from the clear solution by acetic acid.

The *second* is prepared from albumen by a very weak potash-ley at a low temperature. It is not obtained from fibrin, nor probably from hair, as was proved by Tilanus (Scheik. Onderz., Deel III., p. 297), nor from horn. I do not venture to state in what manner a strong potash-ley produces anhydrous protein from substances not affording the hydrate, by means of a weak ley. If, for instance, horn and hair contain some oxide of protein, and the anhydrous form is obtained from them, they must have lost oxygen by the action of a

stronger alkaline ley. Horn and hair, at least, contain no protein, but bi-oxide of protein (The Chemistry of Veget. and Anim. Physiol., Part Third); and as they yield anhydrous protein when treated with a strong alkaline ley, de-oxidation must have taken place.

Although I cannot explain this fact, still it is certain, that substances which contain bi-oxide of protein, instead of protein, yield anhydrous protein when treated with a strong alkaline ley, at an elevated temperature.

It is by no means unimportant which substances are selected for the preparation of protein. No one indeed could suppose that *all* substances containing protein would yield it in a *pure* state, after treatment with an alkali, and the addition of an acid to the solution. I have already stated elsewhere (The Chemistry of Vegetable and Animal Physiology, Part Third), that neither horn nor hair are fit for this purpose; and, without doubt, other substances will be found containing protein, from which it cannot be separated at all, at least in a pure state. It is necessary here to point this out more particularly, that the fact may not be excluded from the science.

In the first place, therefore, those substances are unfit for yielding hydrate of protein which contain the bi-oxide, because — though they also contain protein, — they will yield a mixture of this substance with the bi-oxide. To this class belong horn and hair, which will not yield protein pure, at least until we have discovered a method of separating it from the bi-oxide. The fibrin of blood is similar in this respect to horn and hair. I have, nevertheless, obtained protein from it, although in an anhydrous state. Scheerer has also obtained it. When a stronger alkaline ley is used, the bi-oxide may be converted into protein. This takes place when, from a large quantity of fibrin, only a small



precipitate is produced. (Compare what has been said before, p. 60.)

I have not tried whether the crystalline lens, or gluten, or soluble vegetable albumen, will yield pure protein, nor under what form,—whether anhydrous or in the state of hydrate,—it can be obtained from these substances. Scheerer prepared it anhydrous from the crystalline lens. (*Annalen der Chemie und Pharmacie*, vol. xl.)

I have obtained it from insoluble vegetable albumen, in a pure state, as I think, except, perhaps, that it may have contained a trace of sulphur (*Bulletin*, 1838, p. 112). I have obtained it perfectly pure both from casein and from albumen, either anhydrous or as an hydrate, according to circumstances, as I have mentioned above.

It will henceforth, therefore, be a matter of importance in the preparation of protein, to decide what substance should be employed, since the bi-oxide of protein  $C^{40} H^{30} N^5 O^{14}$  ( $C=75.12$ ) has been found in several instances. This bi-oxide, like protein itself, is soluble in an alkaline ley of moderate strength, and may be precipitated from it by acids. Liebig asserts that he has been unable to procure protein possessing a constant composition; but this may partly have arisen from his not having thought it worth while to pay attention to the bi-oxide, which was first prepared in his laboratory by Scheerer, whilst analyzing hair (*Annalen*, 1840, October), which has been more closely examined by Van Laer (*Scheik. Onderz.*, Deel I., p. 167), and has often enough been dwelt upon by myself. (*Scheik. Onderz.*, Deel I., p. 550.—*The Chemistry of Animal and Vegetable Physiology, &c.*)

I have no doubt, however, that Liebig, on finding this bi-oxide of protein more frequently, will use it as an argument against protein itself, and thus obtain

a new weapon for the combat. He is welcome to do so. If his remarks are correct, I shall be grateful for them; but I myself am of opinion that the fact, that  $C^{40} H^{30} N^5 O^{14}$  (bi-oxide of protein) may exist either with or without an additional atom of hydrogen is a further confirmation of the existence of  $C^{40} H^{30} N^5 O^{12}$  (protein). (The reader will remember that the diminution of the equivalents of hydrogen by one is caused by the difference in the equivalent weight of carbon, which in my first experiments was assumed to be 76.437, and now 75.12.)

It is a question of no small importance to determine what difference there may be in the composition of bodies free from sulphur, which are prepared in accordance with the circumstances under which protein is to be expected? I mean, on treating, for a short time, a protein compound with a potash-ley at an elevated temperature, what are the substances with which protein may be rendered impure, or which can take its place? This question may be answered with regard to fibrin, albumen from serum and from eggs, casein, gluten, legumin, soluble vegetable albumen, the crystalline lens, hair, horn, whalebone, and others. By answering this question, an insight is obtained into Liebig's difficulties, that is, the differences which he has found, or, I would rather say, which he *may* have found. The whole depends upon the influences which 1 equivalent of water, or 2 equivalents of oxygen, may exercise upon its composition. But none of the substances here mentioned produce a precipitate when thrown down from their solution in potash by acetic acid other than  $C^{40} H^{30} N^5 O^{12}$ , or  $C^{40} H^{30} N^5 O^{14}$  (protein or bi-oxide of protein), or something between these two.

If the temperature is not raised and the potash-ley is so weak as merely to dissolve the substances with-

out any excess of alkali, then the addition of acetic acid will produce a precipitate which scarcely differs from the original substance, which contains sulphur, and possesses nearly the same properties. In the same manner, these substances may be dissolved in ammonia, and precipitated by an acid.

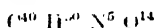
Liebig still persists in the opinion that a body which is nothing else than a mixture of *cellulose* and vegetable albumen, viz., his vegetable fibrin, has the same composition as another which may be dissolved in ammonia unaltered, and precipitated again by acetic acid:—viz., animal albumen. And yet he now asks, not himself, as he first ought to remove this chemical nonsense from the domain of science, but some one else, to reconcile differences which exist in the precipitates from the potash solution; difficulties of which the chief causes have long ago been explained by Scheerer, Van Laer, Van Kerekhoff, Tilanus, and Von Baumhauer, in their treatises upon hair, horn, whalebone, and vitellin.

But whatever precipitate we may obtain from any of the above mentioned substances, it will always be a body free from sulphur, which will possess the main properties either of protein or of bi-oxide of protein, or of these two substances mixed, provided the action of the alkali has not continued too long. We have gradually learned which substances may be most advantageously used, and which avoided, and under what circumstances they must be treated with the alkali. If Liebig *will* not distinguish, if he will not notice what is written, then I ask him at least to make better investigations in this obscure, this *difficult* part of science. A man who boldly attacks me with the assertion that every protein compound when treated with potash under every circumstance ought to yield protein, must have thought himself above reading what was printed on this subject, and

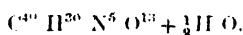
has not scrupled to cast a random difficulty in the way of another, that by lessening him he might exalt himself. Such conduct, in my opinion, is opposed to morality.

The *third* substance mentioned in our list has not been discovered.

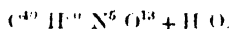
The *fourth*. According to Von Baumhauer (Scheik. Onderz., Deel II., p. 291), the substances which I have formerly described under the name of bi-oxide of protein, and represented by the formula ( $C=75.12$ )



must now be considered as



It is difficult, in the analysis of these bodies, to be certain about 1 equivalent of hydrogen. Fibrin contains

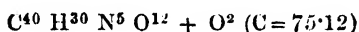


The *fifth* substance can be obtained from hair and horn, by first precipitating protein with a little acetic acid, filtering the liquid, and then adding acetic acid in excess. There is so great a difference between the quantities of the acid that are required for producing these two precipitates, that there need be no fear of an intermixture of the one with the other. Besides, protein is soluble in an excess of acetic acid.

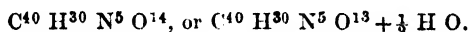
Another mode of preparing this substance is to boil fibrin in water; the whole or the greater part of the sulphur is then separated from the organic combination (Scheik. Onderz. Deel II., Part Third). I do not venture to decide whether the substance that exists in vitellin, and in a soluble state also in serum of blood, belongs to the fourth or fifth of the above substances. This point requires farther investigation.

Should Liebig now deny that these bodies exist,

because differences occur in their several properties (*Annalen*, January 1846, p. 130), I ask him to shew what difference there is in the properties of the present substance, obtained by different methods, both from hair and horn. But if he still denies that they belong to the class of bodies which is represented by the formula



a class which, although closely related to protein, is yet different from it ;—if he denies that there are several bodies of this composition, of which the several properties are diverse, like, for instance, those of cellulose and mucilage ;—it is for him to adduce proofs in support of his opinions. I myself have drawn attention (*The Chemistry of the Vegetable and Animal Physiology*, p. 303, note) to the sulphur that is present in vitellin, as shewn by Von Baumhauer's experiments, and yet I do not hesitate to consider vitellin, although it contains sulphur, as having not the formula of protein, but either,



In the same manner fibrin, according to my more recent investigations, contains,  $C^{40} H^{30} N^5 O^{14} = C^{40} H^{30} N^5 O^{13} + H O$  ( $C = 75 \cdot 12$ ). The presence, therefore, of sulphur in the precipitate, obtained by adding carbonate of ammonia to a solution of fibrin in hydrochloric acid (*Liebig*, in *Annal.*, January 1846, p. 130),—a fact which I have never denied,—proves only that the precipitate is not pure oxide of protein, not that it does not contain it. I therefore still call this body oxide of protein, but add at the same time, that it contains sulphur. I shall return to this substance below. *Liebig* would have done good service, had he enlarged our knowledge

of these substances; "for," as I have said in my work on the Chemistry of Veg. and Animal Physiology, "that knowledge is still in its infancy." But these substances cannot be made to disappear by mere verbal controversy.

It is remarkable, that Liebig, who heretofore has insisted upon the identity of all these substances, and who would not even hear of the presence of sulphur, should now choose to refuse the name of oxide of protein to a body, precipitated by carbonate of ammonia from a solution of fibrin in hydrochloric acid, because it contains some sulphur. He is now right, so far as he repeats what Von Baumhauer and Tilanus have said about vitellin and horn (Scheik. Onderz., Deel III., p. 287 and 307). He might have seen, from the analytical results of these chemists, that when communicating my former investigations of the precipitate from the solution of fibrin in hydrochloric acid, I could not have meant that it contained no sulphur, but merely that I had not then determined it.

The composition of fibrin being now better understood than before, I must modify my former statement respecting this precipitate, viz., that it is produced by the absorption of oxygen from the air. I shall presently enquire whether it contain the same quantity of sulphur as, according to Liebig, fibrin contains (Annalen, January 1846, p. 131).

The *sixth* substance is still unknown.

The *seventh* is obtained by heating chlorite of protein with strong caustic ammonia. It is coloured like anhydrous protein, when it is prepared from hair.

The *eighth* substance is colourless, and is obtained either by boiling fibrin or albumen in water, or from the inflammatory coat of the blood (Scheik. Onderz., Deel I., p. 567, *et seq.*). It may be prepared in large quantity,

by pouring very weak ammonia upon chlorite of protein, when still moist. The chlorite is dissolved, and on evaporation to dryness and digestion in alcohol, this substance is left (Bulletin, 1839, p. 404). If prepared by boiling fibrin, albumen, or the inflammatory coat, it must afterwards be heated with alcohol, in order to dissolve an extraneous substance with which it is mixed. It is obtained in an insoluble form from horn, by means of acetic acid (Tilanus, in Scheik. Onderz., Deel III., p. 307), and also from chlorite of horn, prepared by ammonia and acetic acid (Tilanus, *ibidem*, p. 310).

After these details, it will not be considered superfluous to mention a few particulars respecting casein, albumen, and fibrin. Our knowledge of these substances, however, advances slowly.

## VII. On Casein.

When cow's milk is coagulated by the addition of acetic acid at an elevated temperature, filtered, and the curd washed with dilute hydrochloric acid to dissolve the phosphates, the liquid that passes through, when treated with carbonate of ammonia, yields a precipitate which is mixed with an organic substance.

When the curd that remains on the cloth is washed with water for some time, it gradually dissolves. If mixed with a large quantity of water before it acquires a gelatinous appearance, being nearly freed from acid, and then digested at a temperature of 95° to 104° F., it is completely dissolved in the space of two days. The butter floats on the top, and can be removed. When the liquid is passed through a filter, it becomes perfectly clear, and on the addition of a *very small*

quantity of carbonate of ammonia, yields an abundant precipitate. After this has been separated by filtration, and hydrochloric acid is added to the liquid, a second precipitate is produced, which differs from the first, and has all the properties of hydrochlorate of protein (Bulletin, 1839, p. 21). The hydrate of protein, which I have now found free in this substance, has been pointed out by me before.

The first precipitate may not only be obtained by carbonate of ammonia, but also by water, or by an excess of hydrochloric acid. It is dissolved in an excess of carbonate of ammonia, and is thrown down again by the addition of acetic acid.

The second precipitate is soluble in water, and must, on that account, be washed with alcohol, like the hydrochlorate of protein.

According to these experiments, therefore, milk contains three different substances, which, after its coagulation, are soluble in dilute hydrochloric acid, at the temperature generally employed for digestion. The first of these substances has not been further examined; the second is probably the integument of the milk-cells. It was not necessary to render this insoluble by acetic acid and heat, because it was insoluble of itself, and contained the butter.

The third substance exists in milk in a soluble state, and can be coagulated by means of dilute acids and heat. It may also be rendered again soluble.

The precipitate produced by hydrochloric acid is transparent when dry; that obtained by carbonate of ammonia is white and powdery. The former contains hydrochloric acid.\*

\* The separation of the butter after churning, consists in its emission from the cells in which it is enclosed; whilst the separation of the cream is the rising of the cells to the surface.



The substance obtained from casein by precipitation with carbonate of ammonia, differs from another body obtained in a similar way from fibrin and the albumen of eggs. When fibrin from ox-blood, newly prepared, is treated with dilute hydrochloric acid, it instantly becomes gelatinous, and is dissolved. From the solution, carbonate of ammonia throws down an abundant precipitate, which is soluble in an excess of this reagent. Water does not precipitate it, and, consequently, it differs from the substance found in milk. When this precipitate is separated by filtration, and hydrochloric acid is added to the clear liquid, nothing is thrown down.

Fibrin differs, therefore, from the two substances that are present in milk, and are coagulated by acetic acid.

After fibrin has been kept in alcohol for some time, and is then digested in hydrochloric acid diluted with very little water, it is not dissolved. Fibrin, therefore, is changed by the action of alcohol.

Albumen from eggs is also insoluble in dilute hydrochloric acid. Small pieces of this albumen, which had been thus digested at  $95^{\circ}$ — $104^{\circ}$  F., without being dissolved, became soluble in the same liquid on the addition of a small portion of a pig's stomach. Neither water nor strong hydrochloric acid cause a precipitate from this liquid; but carbonate of ammonia produces one in large quantity. When this is separated by filtration, and the clear liquid treated with hydrochloric acid, no precipitate is thrown down. The substance, therefore, which is present with the casein, is here also wanting. Casein, therefore, as far as it has yet been examined, must consist of three different substances, whereas fibrin and albumen have not yet been shewn to be mixtures. (See p. 98.)

Dumas asserts (*Comptes Rendus*, 29th September 1845, p. 717) that the butter is enclosed in cells. He founds this assertion on the following experiment. According to him, milk, when shaken with ether, does not yield any butter; but if it is previously boiled with acetic acid, ether extracts from it the whole of the butter, and the milk which is separated is now no longer white. If any one will repeat this experiment, he will find the result to be different. When ether is shaken with milk it takes out a great part of the butter. This is, however, no proof that the butter is not enclosed in cells, as has already been remarked by Henle, in his *Allgemeine Anatomie*, p. 943.

When milk is saturated with common salt, the serum may be filtered clear, holding in solution casein, milk, sugar, and salts. The milk globules remain upon the filter. After protracted washing with a solution of common salt, Dumas still found *une matière caséuse associée au beurre de ces globules, et conséquemment insoluble dans l'eau salé*.\*

On repeating this experiment, my results were as follow:—Milk is mixed with an excess of common salt, and the liquid filtered; it comes through clear. The milk globules on the filter are washed with a saturated solution of common salt.

Hydrochloric acid causes turbidity in the liquid. When filtered and heated, a large precipitate appears again. Milk, therefore, contains substances of the protein class; one of them remains upon the filter, and the two others pass through it. The last mentioned substance, however, I have not invariably found; on

\* According to Dumas, casein should now contain 16.5–16.6 per cent. of nitrogen, *l. c.* p. 716. I have thought it unnecessary to repeat this experiment; this result, as well as that from fibrin, is owing to an error in the analysis.

repeating the experiment, I could not always obtain a precipitate by heating. From the liquid, which was filtered perfectly clear from the cream, a precipitate was thrown down by hydrochloric acid. When again filtered clear and heated, it was not at all, or scarcely at all, disturbed.

The snow-white precipitate produced by hydrochloric acid, was not completely soluble in carbonate of ammonia and water. On filtration, however, the quantity which remained upon the filter was too small for examination. Its colour was grey.

When the clear and more or less coloured liquid (which passed very slowly through the filter) was mixed with a little alcohol, a perfectly white precipitate appeared. A very considerable quantity of alcohol could be added before any further precipitate appeared, but at last a very large additional quantity was thrown down.

What has been called casein, therefore, consists of several different substances. Professor Schlossberger, who has made preliminary mention of some of these facts in the *Annalen der Chemie und Pharmacie*, April 1846, p. 92, is engaged in the further investigation of them.

### VIII. *Of Albumen.*

Albumen, like casein, requires a closer investigation. Hitherto no one has endeavoured to separate it into dissimilar constituents, and yet it is possible that such are contained in it.

As regards the quantity of sulphur in albumen, Liebig wrote me in the before mentioned letter, that my determination was entirely incorrect. Six times as much (*six times*, he repeated) as I had found, had been discovered in Giessen. "All the determinations of sul-

phur in all the organic substances, which I had examined, were *false*."

I will take this opportunity to refer to what I have formerly done on this subject, and what I have said about the sulphur.

In the first place, I have been accustomed to oxidise the organic matter and sulphur with nitric acid, and then to add chloride of barium. It appears that the sulphur, which is present in these bodies, is capable of being oxidised in this manner; but the question is, whether the *whole* of the sulphur can thus be oxidised? This question has become one of importance since Redtenbacher has made his investigations on taurin.

I found by this method (Natuur-en-Scheikundig Archief, 1838, p. 87), in albumen from serum 1.00—0.69—0.78—0.74—0.72—0.74—0.82 per cent. of sulphur. The quantities were different, according as *cold* or *hot* water was used in digesting the albumen.

Albumen from eggs gave of sulphur, 0.75—0.66—0.59—0.49—0.43—0.42; the differences arising from the same cause.

I determined the *sulphuric acid* of the *sulphates* that are present in albumen, by digesting it in hydrochloric acid, and adding to the solution chloride of barium. This sulphuric acid I *subtracted* from that obtained in the whole albumen, and introduced in the published formulæ the *smallest proportion* of sulphur among those mentioned above. I concluded by saying, at the place mentioned in the Archief of 1838, "This proportion of sulphur—the mean of 0.46 per cent., which I introduced into the result of my analysis of albumen,—is not the same as that which exists in the white of eggs. During the operation, part of the sulphur has been removed, *the sulphur thus determined, there-*

*fore, is not the whole quantity.* The white of eggs has an alkaline reaction caused by the presence of soda, for when eggs are boiled in the ordinary manner, sulphuret of sodium is separated. Silver, placed in the white of eggs before it is coagulated, does not blacken, but it blackens as soon as coagulation has taken place. *This is known to every one who has eaten an egg with a silver spoon.*" (This I wrote in 1838.)

This shews, therefore, that I have calculated in my formula only the quantity of sulphur which was left in the white of eggs after coagulation, digestion in water, and subtraction of the sulphuric acid of the sulphates. This certainly was an error, but one which all others had up to that time committed along with me. No one understood at that time the condition in which the sulphur of these bodies existed. I endeavoured to reduce its proportion to a minimum, and therefore I burned the albumen with oxide of copper.

If my maximum is now assumed, Liebig ought to shew the presence of 4·5 per cent. of sulphur in the albumen of the blood; but if my minimum, he has to make up only 2·52 per cent. "It (my determination) must be *six times greater.*" Experience will shew who is nearest to the truth.

I must not omit, however, to remark, that, in the determination of sulphur, by means of nitric acid, results are obtained which are a little below the true proportion. Owing to the rather large quantity of nitric acid which is employed, a little of the sulphate of baryta is held in solution. I, therefore, acknowledge that the quantity of sulphur, as represented by my determination, is somewhat too small. We do not yet possess a proper method for determining such extremely minute quantities of sulphur. Redtenbacher, when determining its proportion in taurin, obtained differ-

ences in his results, which are almost as great as the whole of the sulphur that is present in the substance in question, for they amounted to 0·8 per cent.

When the method of burning in a mixture of nitrate and carbonate of potash is employed, the quantity of sulphur obtained is larger; and I willingly prefer this method, although it may and must still be improved.

1·316 grms. of albumen from sheep's blood, exhausted by *cold* water, and dried at 266° F., gave 0·102 sulphate of baryta, equal to 1·07 per cent. of sulphur.

In my former experiments, the maximum was 1·00 per cent.; the minimum 0·69 per cent.

1·141 grms. albumen from eggs, washed with *cold* water, and burned with nitrate and carbonate of potash, yielded 0·105 sulphate of baryta = 1·27 per cent. of sulphur. My former experiments gave 0·75 and 0·66 per cent., when the albumen was washed with *cold* water. This is certainly a considerable difference, great enough to demand attentive consideration.

Admitting that the process of burning with nitre and carbonate of potash yields an amount of sulphate of baryta greater than that obtained on decomposing the organic matter by nitric acid,—because the solution being only slightly acid, less sulphate of baryta will be held in solution than when nitric acid is employed—still this explains neither the present differences in my determinations of sulphur, nor those in my former experiments.

This has led to a new examination of albumen, from which it appears, that as it exists in eggs, and is precipitated by alcohol, it must either be a complex body, consisting of, at least, two different substances containing sulphur, or that it must contain a very large quantity of sulphates.

Albumen, obtained by coagulation, in which state

we have hitherto analysed it, consists partly of protein, formed by the action of carbonate of soda (derived either from the serum or from the liquid in the egg) upon combinations of protein with sulphur. Small differences in the proportion of the alkali cause equivalent differences in the quantities of protein produced, and in the sulphur which forms sulphuret of sodium and hyposulphite of soda. After albumen has been coagulated, therefore, it does not contain a constant proportion of sulphur; and this sulphur partly belongs to undecomposed albumen, partly to the hyposulphite of soda, and partly to the sulphite or sulphate of soda produced.

The subject of albumen, therefore, requires an entire revisal, especially since we know that it consists partly of protein. The investigations that I have commenced on this subject are not yet sufficiently advanced for publication; but I may give this preliminary notice, that that portion of the albumen which can be united to oxide of copper, on being burnt with nitre and carbonate of potash, does not yield more than 1·3 per cent. of sulphur. The salt of copper mentioned below was prepared in the following manner in two successive operations.

Albumen was mixed with water and the liquid filtered through paper. Neutral acetate of copper was then added, the precipitate washed with water, and dried at 266° F. The salt, which had a dark green colour, was burned with nitre and carbonate of potash, dissolved in weak nitric acid, and the solution precipitated with chloride of barium.

I. 1·908 grms. gave, after combustion, 0·049 of insoluble residue, which was oxide of copper, &c.; 1·8 gr. gave 0·187 of sulphate of baryta; 2·492, from the same preparation, gave 0·200 of sulphate of baryta.

II. 1·936 grms. of the second preparation left 0·066

oxide of copper, &c. ; 1·376 yielded 0·133 of sulphate of baryta.

This, therefore, indicates the proportion of sulphur in two portions of the organic substance combined with oxide of copper, to be

I.	II.	Mean.
1·38	1·13	1·30

There is no reason here for any other assumption than this, that the albumen, or the part of it that can be united with oxide of copper, contains 1·3 per cent. of sulphur. Now albumen, *which had lost part of its sulphur* by coagulation, when burned with nitre in the same manner, had yielded the same proportion of sulphur, and therefore a close investigation was necessary to determine which substance was the cause of the large proportion of sulphur in the coagulated albumen. It was proved that this substance, under the circumstances, could not be combined with oxide of copper.

At present I cannot give any further information on this subject, but I think I have reason to believe that the body which we now call *albumen*, contains 1·3 per cent. of sulphur. While, therefore, Liebig asserts, that the quantity of sulphur which he found in albumen amounts to 2·52 or to 6 per cent.,—I allude to my minimum and maximum,—I, on the contrary, hold, that albumen contains only 1·3 per cent. of sulphur, but that a further account must be given of the additional quantity which is also present in the albumen of eggs, and in the serum of blood. Investigations on this subject, however, have been commenced, and an account of them will be given at a future period. I myself, in 1838, drew attention to the imperfect method by which my determinations of sulphur were then made, and every impartial man who chose to oppose them ought to have procured the original memoir, that he



might see what I myself had said upon the subject. It is only now that I have distinctly satisfied myself that boiled albumen consists partly of protein, with sulphuret of sodium and hyposulphite of soda, both of which can be washed out—partly of hypo-sulphurous, sulphurous, or sulphuric acid, combined with protein, which are left behind unchanged,—and partly of unaltered albumen, or perhaps of one or more substances containing sulphur, which are coagulated along with the albumen, and are not precipitated by acetate of copper. If, now, Liebig determines the whole of the sulphur together, then, although obtaining much more than I did, his results are no better than mine were eight years ago. This, then, certainly cannot be called an enlargement of science.

Albumen, therefore, like casein, is probably a complex body; and should this view be confirmed, then there is an additional ground for doubting the similarity between animal and vegetable albumen, which Liebig, without ever having mentioned, and without being able to adduce experiments in support of his belief, has boldly asserted *to be absolutely identical, even with regard to the proportion of sulphur that they contain*. The serum of the blood contains a larger quantity of sulphuretted substances than albumen. When the serum is coagulated, protein is produced, and a certain variable proportion of sulphur is separated, which remains behind in the state of hypo-sulphurous acid, free sulphur, &c., and is either combined or mixed with the protein.

We know, then, regarding the constituent of eggs which can be combined with oxide of copper, that it contains 1.3 per cent. of sulphur. But this is the limit of our knowledge on the subject. The albumen from the

serum of the blood must include the white blood corpuscles, the products of globulin, and perhaps also casein.

I repeat, therefore, that we advance slowly in the knowledge of these bodies, but that hitherto we are not indebted to Liebig for any addition to that knowledge.

What we know of the way in which protein is produced from albumen and other substances, by the influence of a weak alkaline solution at a certain temperature, opens a new field of inquiry as to the influence of temperature on warm-blooded animals, as to the proportion of alkaline salts in their blood, and as to the production of hair, horn, and other protein compounds that contain much sulphur. If in the human body at about 100° F., through the influence of the alkali in the serum of the blood, a part of the sulphur separate from the substance which produces albumen or fibrin,—then there will be an uninterrupted production of protein in the blood, as long as any alkali remains uncombined. I hope to resume the subject on some future occasion.

### IX. *Of Fibrin.*

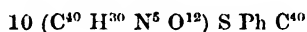
In my first analyses of fibrin, I obtained less carbon than in my last. I shall here transcribe the results of these analyses, which are published in this Bulletin of 1838, p. 107 (C = 76.437).

C	53.40	53.37	53.26	53.48	52.98
H	6.83	6.84	6.95		
N	15.46	15.47	15.72		

I rejected these results, however, and preferred those of another analysis (Bulletin, 1838, p. 108), viz. :—

C	54.46
H	6.90

I thought the latter result might be regarded as representing the true composition, because I had mixed oxide of lead with the oxide of copper, and thus facilitated the combustion of the phosphoretted and sulphuretted substance. Consequently, I assumed fibrin to be represented by the formula ( $C=75\cdot12$ )—



Has Liebig, in analysing a substance, never obtained various results? If necessary, I might compare all those which he has made together. At present, I shall confine myself to quoting those regarding tannic acid from the salt of lead, from which he has calculated the composition of the acid (*Annalen der Chemie und Pharmacie*, vol. xxvi., p. 130).

Tannic Acid.				
	Found.	Per Cent.	Calculated.	Per Cent.
C	20·541	56·78	21·09	58·84
H	1·110	3·08	0·85	2·62
O	14·519	40·14	13·81	38·54
Pb O	63·830		64·15	

If another obtains differences in his results to a much smaller extent than these, he is branded as a clumsy experimenter, but Liebig allows himself to make an error in the carbon of upwards of two per cent. When, in the latter part of last year, I made some ultimate analyses, in concert with my friend Professor Schlossberger, we also analysed a quantity of fibrin, that was as white as lime, and we then obtained results corresponding with my first, as follows:—

Per cent. of ash = 1·11.

0·629 - 6 = 0·623 gave 1·2035 carb. acid, and 0·3885 water.

0·663 - 6 = 0·657 gave of nitrogen

55 cub. cent. before the experiment at 55·850° and 747·7 millim.

139 cub. cent. after the experiment at 50·7° and 749·4 millim.

C = 76.437	C = 75.12
C 53.54	52.66
H 6.93	6.93
N 15.51	15.51*

It appears, therefore, that too much carbon had been obtained in my last analyses (p. 99), arising either from a larger quantity being really contained in the substance, or from an error of analysis.

On repeating the analysis once more, I found

0.336 yielded 0.003 of ash.

0.504 - 5 = 0.499 gave 0.958 of carb. acid, and 0.309 of water.

C	52.50
H	6.88

I was, therefore, mistaken in rejecting my first five analyses, in favour of one which I made later, and I feel happy that this error is corrected.

Fibrin must, consequently, be removed from the class of substances containing protein, and classed among those which contain oxide of protein. Dumas and Cahours (*Ann. de Chem. et de Physique*, tome. vi., p. 404) obtained less carbon, but more nitrogen from fibrin than from albumen. As to the first result, therefore, they are correct, as to the latter incorrect. They found (C = 75.)

C	52.8	52.5	52.7	52.7	52.7
H	7.0	7.0	7.0	7.0	6.9
N	16.5	16.5	16.6	16.6	16.5

We also perceive that the analyses of fibrin made by Scheerer (*Annalen*, 1841) are incorrect as regards the carbon. They gave (C = 76.437.)

C	54.45	55.00	54.98
H	7.07	7.22	6.87
N	15.76	15.82	15.91

\* They have already been communicated by Schlossberger, in *Annalen der Chemie und Pharmacie*, April 1-46, p. 95.

It is clear that these results do not affect the character of fibrin, so far as to remove it from the protein class. Still it now appears to be a peculiar body. In order to become more accurately acquainted with it, it was necessary to repeat the determination of the sulphur, as I had done with the albumen. I will, however, first mention what I had before found. Fibrin, in the state in which I subjected it to an ultimate analysis, viz., exhausted by warm water, yielded only 0.34 per cent. of sulphur, whilst it gave 0.63 per cent. when treated with cold water. My former experiments are as follow:—

Fibrin digested in *cold* water, and decomposed by means of nitric acid, gave 0.63 per cent. of sulphur.

Digested in warm water, and subsequently in alcohol, it yielded by the same process 0.34–0.37 per cent. of sulphur; and digested in warm water, but not in alcohol, it gave 0.50 per cent. of sulphur (Nat. en Scheik. Archief, 1838, p. 93).

I therefore calculated the per-centage of sulphur as 0.36.

By the process of burning with nitre and carbonate of potash I obtained from fibrin, after being washed with cold water, and dried at 266° F., the following results:—

0.686 fibrin from ox-blood gave 0.048 of sulphate of baryta.

1.952 of another kind of fibrin from ox-blood gave 0.158 sulphate of baryta; that is in 100 parts,

0.96

1.12

In this case, also, I obtained more by burning with nitre than by decomposition with nitric acid, and I consequently admit that I have represented the sulphur in fibrin as well as in albumen by too low a figure. Although I had before found 0.63 and 0.50 per cent..

yet I had assumed the smallest per-centage, but even taking the largest quantity, the nitric acid process yielded too little. This method should therefore be rejected.

It was an error to apply it here, since a small difference was of much importance. But did not I share in this error with the most experienced chemists? Would not every reasonable and honest man naturally have recourse to the defective method? Must it be called a *false* result, if a method, that is generally considered as correct, produces a quantity that is somewhat too small? In this case almost all the determinations of hydrogen in organic analyses are *false*, for we find in nearly every instance more than the substance actually contains.

The method of burning with nitre and carbonate of potash cannot, because of its defects, lead to an entirely correct determination of the sulphur. Thus our new determinations are again false. The extremes which Redtenbacher obtained from taurin, were 25.99 and 25.20 of sulphur, which is a difference of 0.79 per cent., approaching to the entire quantity present in fibrin (*Annalen der Chemie und Pharmacie*, February 1845, p. 172). I shall not call these results false, but, on the contrary, I consider Redtenbacher, as every one else does, to be an excellent experimenter.

I, however, committed an error in this case, because in my former analyses of fibrin, as in those of albumen, I not only *mention* the *lowest* quantity of sulphur that I found—the whole of my determinations, however different, were published,—but also *calculated it in* the formula.

But we are still to decide the question, what place must be given to fibrin in the class of the protein compounds? While assuming 75.12 as the equivalent weight of carbon, we cannot at present represent it as regards

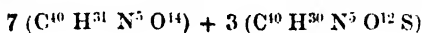
the carbon, hydrogen, nitrogen, and oxygen, by any other formula than,—

	Atoms.	Calculated
G	40	52·88
H	31	6·84
N	5	16·60
O	14	24·68

The small difference between the proportions of carbon found and calculated is made up by the quantity of sulphur and phosphorus present in the fibrin analysed. The composition of the substance in the state in which it was analysed—probably its normal condition—was (C=75·12).

	Found.
C	52·66
H	6·93
N	15·51
O	23·53
S	1·04
Ph	0·33

The formula, therefore, which I formerly gave for protein requires modification. I must leave undetermined in what state the phosphorus is contained in it. Neither shall I endeavour to give a more correct explanation of the condition in which the sulphur exists in fibrin, because I cannot adduce any proof in support of it. But since the sulphur of fibrin, like that of albumen, is completely eliminated when the substance is properly treated with potash, and since, nevertheless, a group of the four elements (C, H, N, and O), which admits of being represented by the formula (C<sup>40</sup> H<sup>30</sup> N<sup>5</sup> O<sup>12</sup>), may be precipitated from the solution, the sulphur must, in a part of this substance, take the place of oxygen. As an example of one way in which this may be explained, I offer the following scheme



The sulphur may be in a similar condition in albumen. I have given examples of similar formulæ in the cases of horn, hair, and whalebone—(The Chemistry of Vegetable and Animal Physiology). I hope no one will suppose that I regard this formula as established. I myself would have to ask, where I had obtained any certain proof of its accuracy. I wrote in the places quoted, “that our knowledge of these substances is still in its infancy.” I should feel grateful to any one who would advance that knowledge. It must therefore be from the substance indicated by the second part of the above formula, that the protein obtained by means of potash is derived; whilst that which is represented by the first part is probably held in solution, and cannot be precipitated by acetic acid, but by chlorine alone.

Albumen, of which the formula must also be altered in consequence of the increase in its proportion of sulphur, is possibly composed of two other groups, regarding which I hope to give an account at a future period.

The production, therefore, of fibrin from albumen, and from other bodies which contain the substance represented by the formula  $C^{40} H^{39} N^5 O^{12}$ , takes place under the influence of oxygen. And thus it may be considered as proved, that there is NO VEGETABLE FIBRIN;—that there is no foundation whatever for the similarity asserted by Liebig between animal fibrin and coagulated vegetable albumen, which he calls *vegetable fibrin*. It is merely a mixture of an albuminous body with cellulose and the other parts of wheaten-flour, which are insoluble in water and alcohol. Plants, and especially seeds, in which every process terminates in de-oxidation, cannot be imagined to contain any hydrate of the protoxide of protein.



Whatever name may now be given to this body, it contains more oxygen than the hydrate of protein.

We have seen above (p. 34), that Liebig has boldly asserted, that animal fibrin and *his* vegetable fibrin (or the mixture of cellulose and an unknown albuminous body, which we usually call *coagulated vegetable albumen*) contain the same proportion of sulphur. Science has never received any proofs of this assertion, and never will receive them. Liebig cannot procure any such proofs, since vegetable fibrin has no existence. There can be no similarity in the proportion of sulphur between a *non-existing* substance and the fibrin of blood. Vegetable casein and vegetable fibrin have, therefore, ceased to exist. As regards the similarity between vegetable and animal albumen, which has likewise been boldly proclaimed by Liebig, we are even to this day waiting for proofs of this assertion. This assumed similarity has for some years been adopted as a fact by every one; but, from what has been said at p. 105, it can no longer be so.

What I have here mentioned is sufficient to explain the statement made at p. 550 of the first volume of the "Scheikundige Onderzoekingen," as to the change which fibrin undergoes on being boiled with water, dissolved in hydrochloric acid, and precipitated by carbonate of ammonia. All these bodies, which are insoluble in water, contain the same proportions of carbon, hydrogen, and nitrogen, as fibrin does, viz., (C=75·12):—

Fibrin.	The same boiled and insoluble in water.*	The same dissolved in hydrochloric acid, and precipitated by carbonate of ammonia.†
C 52·66	52·70	52·69
H 6·93	6·90	6·88
N 15·51	15·63	15·85

\* Scheikund. Onderz., Deel I., p. 568.

† Ibidem, p. 578.

The part which is dissolved when fibrin is boiled in water, consists partly of the hydrate of tri-oxide of protein (Scheik. Onderz., Deel I., p. 507), and partly of another substance soluble in alcohol, in regard to which I shall give some details on a future occasion.

I thought it worthy of a closer examination, whether that part of fibrin which is dissolved in hydrochloric acid, and precipitated by ammonia, contains the same proportion of sulphur as fibrin itself (which is an assertion of Liebig's). The substance was prepared in the manner stated at p. 576 of the first volume of the Scheik. Onderzoekingen. It was dried at 266° F., and burned with nitre and carbonate of potash. I did not look for, and consequently did not determine, the phosphorus.

1.476 gr. burned with carbonate of potash and nitre, yielded 0.114 sulphate of baryta, equal to 1.06 per cent. of sulphur. The quantity of sulphur has therefore not diminished, and Liebig is right here. I thank him for this.

There is, consequently, no difference between the composition of fibrin and that of the precipitate produced by carbonate of ammonia, from a solution of fibrin in hydrochloric acid, except, perhaps, in the quantity of phosphorus, as to which I have made no further investigation. But I nevertheless persist in asserting, contrary to Liebig's statement (*Annalen*, Jan. 1845, p. 130), that the precipitate obtained by carbonate of ammonia from a solution of fibrin in hydrochloric acid, is not oxide of protein. *It is actually this body, but contains sulphur*, as I said two years ago concerning vitellin (*The Chemistry of Vegetable and Animal Physiology*), as analyzed by Von Baumhauer, a statement which Liebig seems to have purposely passed over.

Liebig is right, however, in asserting that the air takes no part in the production of this substance. It is unchanged fibrin,—at least the quantities of sulphur, carbon, hydrogen, and nitrogen, have remained unchanged. For this I also offer my thanks to Liebig. But its organic elements are nevertheless represented very nearly by  $C^{40} H^{31} N^5 O^{14}$  ( $C=76.437$ ). It contains, therefore, bi-oxide of protein, empirically represented by this formula:—If the carbon be assumed to have an equivalent weight of 75.12, this substance is chiefly an hydrate of the protoxide of protein ( $C^{40} H^{30} N^5 O^{13} + H O$ ). Fibrin, as regards its four elements, C, H, N, and O, has thus the same composition as I have previously assigned to the oxide of protein in its insoluble form; nearly all I have said of that substance, therefore, applies to fibrin. It is certain that fibrin is a product of the oxidation of albumen, and is formed in the lungs. Thus there is a real difference between fibrin and albumen; and it appears to me, that the attempts made by Dumas and others, to convert one into the other in the way they have hitherto followed, cannot possibly be successful. So much at least results from the above numbers;—all farther explanation must be left to the future. Liebig's idea, that the substance precipitated by carbonate of ammonia from a solution of fibrin in hydrochloric acid, should not be called oxide of protein because it contains phosphate of lime (*Annalen*, January 1846, p. 131), is one of those objections, by which he shews that persons and not facts are his aim. Does not tartrate of lead contain tartaric acid? Is it wrong to speak of tartaric acid as combined with oxide of lead, because of the presence of oxide of lead? And is a compound of an organic substance with phosphate of lime an organic substance no longer? Is gum-arabic not gum, because it contains a trace of inorganic

matter? Is sugar, as it occurs in commerce, no longer sugar, because it contains a little lime? Remarks of this kind are never made by Liebig without a purpose—they are always intended to undervalue the works of others.

I owe him my thanks for having drawn my attention to the proportion of sulphur which I formerly omitted to determine. I have learnt from this, that fibrin may be dissolved in hydrochloric acid, and precipitated unchanged by carbonate of ammonia. It has become an object of importance, to institute a comparison between fibrin and the several precipitates of casein, of which I have spoken at p. 97, and the substance thrown down by carbonate of ammonia, from a solution of albumen in hydrochloric acid, aided by a fragment of the mucous membrane of the stomach.

I have still to draw attention to a substance with which fibrin may be mixed, and which ought to be noticed in the examination of fibrin. When blood is allowed to coagulate, and the fibrin is then washed out of the clot, it is impossible to remove all the cells of the blood-corpuscles. The colouring matter may be extracted either by alcohol and hydrochloric acid, or by alcohol and ammonia, but the cells just mentioned cannot be thus removed. Fibrin, although perfectly white, may still contain globulin. It is possible that it was this globulin (the cellular membranes of the blood-corpuscles), or, at least, some product of it insoluble in hydrochloric acid, which Bouchardat found to be left behind, during the solution of fibrin. It may be, at least, that what he calls *epidermose* was only a product of globulin (Scheik. Onderz., Deel I., p. 377). In many of its properties it agrees with bi-oxide of protein. It must suffice at present that I

have drawn attention to a possible impurity in fibrin, and to the necessity of beating the blood immediately after it has flown from the animal, lest the fibrin that is obtained be mixed with a large portion of globulin.

Our knowledge of fibrin having thus advanced nearer to the truth, we find in it a regular connection with what we know of the inflammatory coat, and of the muscular fibre.

I have formerly stated concerning this inflammatory coat (Scheik. Onderz., Deel I., p. 560), that when boiled, one-seventh part of it is converted into a soluble substance, which consists in part of the hydrate of tri-oxide of protein, and that the rest remains insoluble, and has the properties and composition of fibrin. This change takes place within a quarter of an hour. Fibrin, when boiled for a long period, yields the same products, although in a different proportion. Consequently, the inflammatory coat is not fibrin, but contains the substance of fibrin.

It is my opinion, based upon the analytical results, mentioned at the place quoted above, that the inflammatory coat may be considered as a combination of the hydrates of the protoxide, and of the tri-oxide of protein ( $C=75.12$ ):—

	Von Baumhauer.	
C	52.10	52.23
H	6.93	7.04
N	15.51	
O	25.46	

No determinations have yet been published of the sulphur and phosphorus; such ought therefore to be made. This body, when boiled in water, is decomposed into  $C^{40}H^{30}N^5O^{13} + H O$ , or  $C^{40}H^{31}N^5O^{14}$ , and  $C^{40}H^{30}N^5O^{15} + H O$  ( $C=75.12$ ), in the proportion of about 6 equivalents of the former to 1 equivalent of the latter. We

have, at all events, seen that the inflammatory coat is not pure fibrin, and must on no account be considered as bi-oxide of protein. Before, however, deciding as to its real character, it is necessary to study it more closely, and to search for other reagents by which its constitution may be discovered.

I have to add another property in which fibrin appears to differ from bi-oxide of protein, that is, from the substance obtained from whalebone, horn, and hair, of which the composition approaches to that of fibrin. This property is as follows. When a current of chlorine is passed through a solution of fibrin in ammonia, the precipitate obtained is composed according to the formula  $C^{40} H^{30} N^5 O^{12} + Cl O^3$ . But when the same operation is performed upon bi-oxide of protein, the product is quite different, and cannot be confounded with the former, having the formula  $C^{40} H^{30} N^5 O^7 + Cl O^3$ . Fibrin therefore may contain  $C^{40} H^{30} N^5 O^{13} + H O$ , but not  $C^{40} H^{30} N^5 O^{14}$  (compare Bulletin, 1839, p. 401, and Scheik. Onderz., Deel I., p. 172, Deel II., p. 400, and Deel III., p. 309). I have not investigated whether this property belongs also to fibrin that has been boiled in water for a long period, or to the precipitate produced by carbonate of ammonia from the solution of fibrin in hydrochloric acid. We do not therefore know with certainty, whether these are represented by  $C^{40} H^{30} N^5 O^{13} + H O$ , or by  $C^{40} H^{30} N^5 O^{14}$ .

### X. *Of the Muscular Mass, and the substance of the Primary Fibres.*

Regarding muscular fibre, I have formerly stated (The Chemistry of Vegetable and Animal Physiology, Part III.), that from a solution of muscle in a weak

potash-ley, Adriani obtained a precipitate by means of acetic acid, and that this precipitate had the same composition as bi-oxide of protein; and, further, that the same substance was obtained by adding carbonate of ammonia to a solution of muscle in acetic acid. After these precipitates had been digested in water, alcohol, and ether, they gave the following results. I shall, however, first mention other results obtained by Adriani from the analysis of muscle in its natural state, which have also been communicated in the third part of my work above mentioned:—

Muscular flesh of a cow at 266° F.  
Per-centage of ash, 0·5.

I. 0·736 - 3 = 0·733 gave 1·414 carb. acid, and 0·477 water.

II. 0·335 - 1 = 0·334 gave 0·645 carb. acid, and 0·220 water.

0·567 - 2 = 0·565 gave of nitrogen—

	Therm.	Barom.
122 cub. cent. before the exp. at 42°·8, and		766·4 millim.
197 cub. cent. after the exp. at 42°·3 F., and		761·6 millim.

C = 76·437,—

	I.	II.
C	53·34	52·92
H	7·23	7·30
N	16·31	
OS	23·12	

Beef, first completely washed with water, then dissolved in a weak potash-ley by the aid of heat, and precipitated by acetic acid, yielded a substance which was treated with alcohol, and dried at 266° F.\*—

0·193 left 0·001 of ash.

0·331 - 1 = 0·330 gave 0·648 of carb. acid, and 0·203 water.

0·654 - 3 = 0·651 gave of nitrogen

128 cub. cent. before exp. at 39° F., and 756·2 millim.

215·5 cub. cent. after the exp. at 44° F., and 758·5 millim.

\* We did not at the time examine whether this body contains sulphur. This solution was made with a ley containing  $\frac{1}{10}$  of dry caustic potash-ley. See my work on Physiological Chemistry.

C = 76.437,—

C	53.83
H	7.11
N	15.38
O	23.68

Beef washed with cold water, dissolved in acetic acid, the solution filtered and precipitated by carbonate of ammonia, and the precipitate washed and boiled in alcohol, gave the following results :—

0.460 left 0.001 of ash.

0.438 - 1 = 0.437 gave 0.852 carb. acid, and 0.281 water.

0.641 gave of nitrogen—

125 cub. cent. before experiment at 61° F., and 758.9 millim.

210 cub. cent. after experiment at 61° F., and 758.3 millim.

C = 76.437,

C	53.91
H	7.15
N	15.24
OS	23.70

The experiments upon the nature of the precipitate obtained by acetic acid from a solution of muscle in potash, we have again repeated. For this purpose, we employed beef and veal, separated as much as possible the pure muscular portion, cut it fine, and washed and kneaded it with water, till it was perfectly white. It was then dissolved in a potash-ley, at a temperature of about 140° F. This solution was exposed to the air, filtered and precipitated by acetic acid, the precipitate washed with water, boiled in alcohol and ether, and dried at 266° F.

The results were as follows :—

*Protein from beef* 0.322 left 0.003 of ash.

- I. 0.711 - 7 = 0.704 gave 1.418 of carb. acid, and 0.444 of water.
- II. 0.541 - 5 = 0.536 gave 1.067 of carb. acid, and 0.349 of water.



$$C = 76.437$$

	I.	II.
C	55.69	55.04
H	7.01	7.23

*Protein from veal* 0.611 left 0.005 of ash.

0.511 - 4 = 0.507 gave 1.017 of carb. acid, and 0.321 of water.

$$C = 76.437$$

C	55.46
H	7.05

We here find exactly the composition of protein, as I have stated it from the commencement, and have now calculated, by assuming 75.12 as the equivalent weight of carbon.

The precipitate, however, may be mixed with a little elastic tissue, but this can have no influence on the results of the analysis.

The difference between these results and those of Adriani is one equivalent of water.

And now I conclude the analytical results of this investigation with that same body, which has formed the axis around which Liebig's pen has revolved,—the removal of which from the world of science would make him extremely happy: I mean that body which is known by the formula  $C^{40} H^{30} N^5 O^{12}$  ( $C=75.12$ ); a substance which I formerly named *protein*, and which I still distinguish by that name, only adding the word *anhydrous*; a substance which neither depreciation of the work of others, nor threats of an ABYSS, can banish from the created world, no earthly power being able to deprive it of reality; a substance, however, with which we are still but imperfectly acquainted, because it is one of the most complex of bodies, of which our knowledge will, therefore, only reach a certain degree of perfection after *all other bodies* are fully known. It has been possible to ascribe a certain scientific value

to the relation which exists between acetic acid and alcohol; and yet we speak of a chlor-acetic acid, which must again overthrow what was considered to be established. But, of the albuminous bodies, he who requires of another a thorough chemical knowledge, without himself exhibiting such knowledge, shews himself to be a stranger to the first rules of humanity. I even state, in so many words, that we know nothing at all concerning the constitution of these bodies. We only know that they possess one constituent in common, which has received the name of protein; and this knowledge, from whatever person it may have emanated, does not admit of destruction.

## XI. *Of the Properties of Protein and its Compounds.*

### *a. Anhydrous Protein, (C<sup>40</sup> H<sup>30</sup> N<sup>5</sup> O<sup>12</sup>).*

It is amber-coloured, or even darker, especially when prepared from hair, or by means of strong alkaline solutions from other protein compounds.

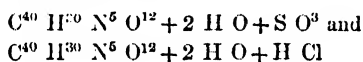
The properties of this substance are described with such detail in the work of Berzelius, that it is unnecessary to add here one word. I must, however, remind the reader that the compounds of protein with metallic bases, there mentioned, must be considered as non-existing, after what I have stated upon this subject at p. 112 of the Bulletin, 1838. All the substances that contain either protein or the two first oxides of it, are united into one group by their common property of forming xantho-proteic acid (C<sup>34</sup> H<sup>26</sup> N<sup>4</sup> O<sup>11</sup>), through the influence of nitric acid; and, further, by becoming purple under the action of hydrochloric acid and oxygen, and by being precipitated from their solutions in acetic acid by prussiate of potash. With strong

sulphuric acid they form a compound, represented by the formula  $C^{40} H^{30} N^5 O^{12} + S O^3$ .

*b. Hydrate of Protein,  $C^{40} H^{30} N^5 O^{12} + H O$ .*

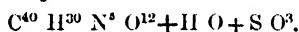
It is affected by various reagents in the same manner as the former substance, but it is more readily soluble in ammonia, acetic acid, weak potash-ley, &c. At 266° F. it does not part with its equivalent of hydrate water, but this can be replaced by chlorous acid, and thus is formed  $C^{40} H^{30} N^5 O^{12} + Cl O^3$ .

When in solution it combines with hydrochloric and sulphuric acids, and forms



—(Bulletin, 1839, p. 21).

I have not examined whether it can combine with the first hydrate of sulphuric acid, and form the compound

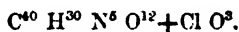


With tannic acid it forms a compound having the formula



*c. Hydrate of Protoxide of Protein,  $C^{40} H^{30} N^5 O^{13} + H O$ .*

The only substance which contains this body, as far as we yet know, is the fibrin of blood; perhaps it also exists in vitellin, and in the inflammatory coat. Its principal properties agree with those of protein, but it is characterised in fibrin, *if this has not previously been in contact with alcohol*, by being very readily soluble in acids. With chlorine it forms a combination, having the formula



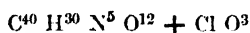
*d. Bi-oxide of Protein, C<sup>40</sup> H<sup>30</sup> N<sup>5</sup> O<sup>14</sup>.*

This compound was first obtained from hair by Scheerer. It has different properties, according to the substance from which it has been extracted. It was described with much detail by Van Laer (Scheik. Onderz., Deel I., p. 168), such as he obtained it from hair. That obtained by Van Kerekhoff from whalebone (Scheik. Onderz., Deel II., p. 393), had the same properties, and J. L. Tilanus also extracted it with the same character from this substance (Scheik. Onderz., Deel III., p. 299). It may be prepared from hair and horn, by dissolving them in potash, and—after the precipitation of any protein that may be present by a little acetic acid—by adding an excess of acetic acid, which causes the precipitation of the bi-oxide. It may be obtained from whalebone by dissolving in strong acetic acid, and throwing down by ammonia. This substance has several properties in common with the hydrate of protein, but it cannot be confounded with it, both because its other properties and its composition are different. For comparison's sake, I will mention here some properties by which they may be distinguished from each other.

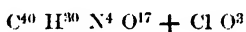
When to an alkaline solution, in which both protein and the oxide of protein are present, a little acetic acid is added, the former is precipitated; but the latter remains in solution, and only falls when an excess of acetic acid is added. Protein is soluble in a large quantity of this acid; and although, therefore, a little of it might at first have been precipitated along with the oxide, there is no danger of their being mixed in any considerable quantity with each other, and, besides, there is a perceptible difference between them.

Protein is insoluble in water, but the oxide is more or less soluble. The former is insoluble, the latter soluble, in very weak acetic acid.

One of the most important differences between these two bodies, is exhibited by the action of chlorine. When a current of this gas is passed through a solution of protein, the compound produced has a composition which is represented by the formula



and when passed through a solution of the bi-oxide, the precipitate has the formula



(Van Laer, Van Kerckhoff, and T. L. Tilanus in Scheikund. Onderz., Deel I., p. 171, Deel II., p. 400, Deel III, p. 309.) This is an important difference. Fibrin, albumen and casein—all of which produce  $C^{40} H^{30} N^5 O^{12} + Cl O_3$ —are distinguished by this property from horn, whalebone, and hair—the substance obtained from these having the formula  $C^{40} H^{30} N^4 O^{17} + Cl O_3$ .

Liebig's assertion, therefore, "that we have recently been presented with so many various substances, which, although most different in properties, are all to be considered as oxides of protein" (Annalen, January 1846, p. 130), does not certainly apply to this body, of which every impartial person will acknowledge, both that it differs from protein, and that it is always one and the same, although prepared from the most different substances, such as horn, whalebone, and hair.

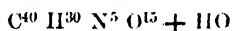
*e. Tri-oxide of Protein,  $C^{40} H^{30} N^5 O^{15} + HO$ .*

Van Laer obtained this body from hair in the anhydrous state (Scheik. Onderz., Deel I., p. 161). He found it to possess the same properties as the hydrate, except that it is a little less soluble in water. In the Bulletin, 1839, p. 406, I have described the proper-

ties of this substance obtained from the chlorite prepared from fibrin, albumen, and casein; and, in the Scheikundige Onderzoekingen, those which it possesses when prepared by boiling fibrin and albumen. I think it unnecessary to repeat all this here.

It is remarkable, that this substance does not form a precipitate with prussiate of potash.

In the insoluble form, Tilanus prepared it from horn, by boiling in acetic acid (Scheik. Onderz., Deel III., p. 307). It gave a precipitate with prussiate of potash, and was composed according to the formula



If Liebig will take the trouble of reading over the various passages I have quoted, he will do well to recall his statement, "that we have recently been presented with so many various substances, which, although exceedingly different in properties, are all to be considered as oxides of protein." We have, at least,—

1<sup>st</sup>, Looked for differences in their properties, wherever bodies have been described under different names; 2<sup>d</sup>, for the same properties and composition in all bodies which have been classed under the same name; and, 3<sup>d</sup>, when the difference in these properties was very small, it has been considered inexpedient to introduce as yet any new names into science, but rather to distinguish the compounds by designations which express their composition as nearly as possible.

I shall persist in following these three rules, whatever objections may be made to them. Liebig alone is capable of asserting that I have not been guided by them in this investigation.

## CONCLUSION.

I believe I have shewn in the preceding observations, 1st, That I am opposed to the spirit which Liebig tries to introduce into the world, and that I consequently avoid it. I warn my young readers against it. This spirit will tend to pull down what is good, and to promote what is bad.

2d, That I have a right, nay that I am bound to accept no more of Leibig's justice. Whatever I may in future produce in the domain of science, is to be considered as *not* written for him. I readily give him liberty to hurry me into the *abyss*.

3d, That I have removed some errors from the history of protein, and that I have enlarged our knowledge of it with some new facts, for which I am indebted to Liebig's desire for controversy.

The evil has thus had a good effect in this case. I shall now quietly proceed in the study of the science which is dear to me, caring little about the attempts of coarse selfishness to mutilate my labours. I will, however, nourish my aversion to people who do not understand the following sentence :

“Ingenuas didicisse fideliter artes, emollit mores nec sinit esse feros.”

## ANSWER TO M. N. LASKOWSKI.

In the *Annalen der Chemie und Pharmacie*, Mai 1846, there has at last appeared an article which had been long expected. You have lent your name to this

article, and perhaps you have partly written it yourself.

My first answer to you is, Read in Otto, or any other work on Chemistry, what takes place, when sulphur is dissolved in potash-ley.

My second is, Let not the small determine the value of the great ; never calculate formulæ from those constituents of a compound which are present in the smallest quantity.

My third is, Be on your guard against your master. He now employs you, as he has formerly done others, to feed his own ambition and desire for controversy. By and by he will reject and calumniate you, as he has done all your predecessors who did not always kneel in the dust before him. Even now I think it doubtful, if he does not already lay snares for you, since he has purposely left you unacquainted with the history of the hyposulphites ; since he has told you nothing of the solution of sulphuret of potassium, and made you operate with silver and oxide of bismuth, to remove the sulphur from an alkaline solution, from which it could not be separated by boiling ?

If I am not mistaken, your master expected the good fortune of killing by *one* blow, Dumas and Cahours, Scheerer, Laskowski, and Mulder. Thus he strikes on, until, in his estimation, no one that has any idea of chemistry shall be left in the world but himself. Take a lesson from the past. Mark how your master employs for *his* purpose *all* that are about him, and how he abuses them, as soon as they are no longer of any use to him. Your fate will be the same. Open your eyes before it is too late. As long as I did not contradict him, he employed Scheerer to confirm all my results ; but now, having made some scientific remarks against him, he employs you and others to proclaim all



my results as false. “ He finds himself opposed to me in *self-defence*, and I must not be surprised, if he tell me in public, what he wrote me in his private letter” (Letter, 29th May 1846). You are therefore to assist him in his contest.

If you persist in your opinions, I shall hereafter give you another reply ; but I have considered it my duty first to warn you, who are young and inexperienced, and have allowed yourself to be employed by a man whom you did not know.

You have exhibited to the world the singular picture of a person at once contesting and confirming the same thing at the same time. But no ! your master has done this, or at least the greater part of it for you, and you have lent your name.

Take my advice, and give your name to better things in future.

G. T. MULDER.

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